

Hitchhiker's Guide to Magnetism

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Definitions and Units

Let's start with a few definitions. There are three magnetic vectors:

- | | |
|-------|--------------------|
| (1) H | Magnetic field |
| (2) M | Magnetization |
| (3) B | Magnetic induction |

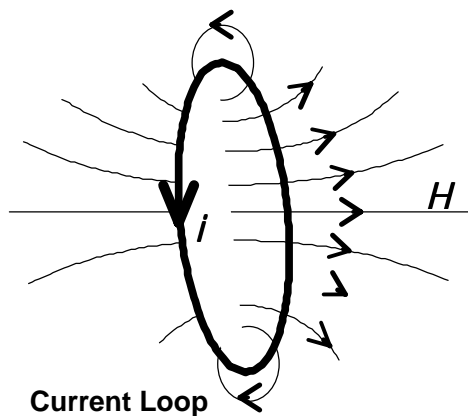
There is some confusion in the literature over units. SI units are now the preferred units over the older CGS . Confusion prevails because there are two ways that magnetostatics is presented:

1. fictitious magnetic poles (CGS: centimeter, gram, second)
2. current sources (SI: système internationale)

As a result, the form of many of the basic equations are different between the two systems. What this all means is that some arbitrary constant has units in one system but is equal to unity and dimensionless in the other system. There are also factors of 4π floating around.

The difference between the pole and current approach is only significant in the subject of units. The older (pre 1980) paleomagnetic and rock magnetic literature is primarily in CGS units.

Because SI are now the units of choice, we begin with current loops. Consider a loop of radius r and current i , roughly equivalent to an atom with orbiting electrons.



A magnetic field H will be produced at the center of the loop given by

$$H = \frac{i}{2r} \quad [\text{Amperes/meter, A /m}]$$

The current loop has a magnetic moment, m , associated with it

$$m = i \times \text{Area} \quad [\text{Am}^2]$$

The intensity of magnetization, M or J , is magnetic moment per unit volume

$$M = \frac{m}{v} \quad [A/m]$$

Note that M and H have the same units.

Magnetic moment per unit mass, σ , is

$$\sigma = \frac{m}{\text{mass}} \quad [\text{Am}^2/\text{kg}]$$

Another fundamental quantity is the ratio of magnetization to magnetic field, which is called the susceptibility

$$\kappa = \frac{M}{H} \quad [\text{dimensionless}]$$

The mass susceptibility is

$$\chi = \frac{\sigma}{H} = \frac{\kappa}{\text{density}} \quad [\text{m}^3/\text{kg}].$$

Susceptibility is a measure of how magnetizable a substance can become in the presence of a magnetic field and can be used in a general way to describe the various classes of magnetic materials. A related quantity, denoted by μ , relates B to H and is called the permeability (Engineering types use permeability instead of susceptibility).

In the SI system, the relationship between B, H and M is given by

$$B = \mu_0(H+M) \quad [\text{Tesla, T}]$$

The B unit is called the Tesla and the total B field is the sum of the H field and the magnetization M of the medium. The constant μ_0 is called the permeability of free space. In SI it is equal to $4\pi \times 10^{-7}$ Henry/m.

However, in CGS, μ_0 is set equal to unity, which makes B and H, and M numerically equal to one another, but each have different unit names (arbitrarily chosen and named after famous dead people, Gauss, Oersted, and emu/cm³). The CGS equation is

$$B = H + 4\pi M$$

Herein lies some of the confusion, because in CGS, B and H are used interchangeably, but the unit conversions going to SI give different numerical values. For example, the earth's field is 0.5 Gauss or 0.5 Oe. However, in SI

$$\begin{array}{ll} 0.5 \text{ Gauss} = 50 \mu\text{T} & [\text{B fields}] \\ 0.5 \text{ Oersted} = 39.8 \text{ A/m} & [\text{H fields}]. \end{array}$$

As you can see from this example, it is much easier to convert Gauss to Tesla (move the decimal point 4 places) than to convert Oersted to A/m. So it is not too surprising that this is the current practice used by paleomagnetists to report all fields (B and H) in Tesla. We have not decided suddenly that the B field is more fundamental than the H field (neither field is any more fundamental than the other). Actually, when we talk about an alternating "field", or a magnetic "field", of say 100 milliTesla (mT), we really mean $\mu_0 H = 100 \text{ mT}$. However, this is rarely noted.

I have summarized the comments about units in Table 1.

Magnetic Term	Symbol	SI unit	CGS unit	conversion factor
magnetic induction	B	Tesla (T)	Gauss (G)	1 T = 10^4 G
magnetic field	H	A/m	Oersted (Oe)	1 A/m = $4\pi/10^3$ Oe
magnetization	M	A/m	emu/cm ³	1 A/m = 10^{-3} emu /cm ³
mass magnetization	σ	Am ² /kg	emu/g	1 Am ² /kg = 1 emu/g
magnetic moment	m	Am ²	emu	1 Am ² = 10^3 emu
volume susceptibility	κ	dimensionless	dimensionless	$4\pi(\text{SI}) = 1$ (cgs)
mass susceptibility	χ	m ³ /kg	emu/Oe· g	1 m ³ /kg = $10^3/4\pi$ emu /Oe· g
permeability of free space	μ_0	H/m	dimensionless	$4\pi \times 10^{-7}$ H/m = 1 (cgs)

A= Ampere
cm= centimeter

emu= electromagnetic unit
g= gram
kg= kilogram
m= meter
H= Henry

For more information on SI and CGS units in magnetism see:

M.A. Payne (1981), Phys. Earth Planet Inter., **26**, P10-P-16, with errata
(1981), Phys. Earth Planet. Inter., **27**, 233.
P.N. Shive (1986), Transactions American Geophys. Union (EOS), **67**, 25.

Classes of Magnetic Materials

The origin of magnetism lies in the orbital and spin motions of electrons and how the electrons interact with one another. The best way to introduce the different types of magnetism is to describe how materials respond to magnetic fields. This may be surprising to some, but all matter is magnetic. It's just that some materials are much more magnetic than others. The main distinction is that in some materials there is no collective interaction of atomic magnetic moments, whereas in other materials there is a very strong interaction between atomic moments.

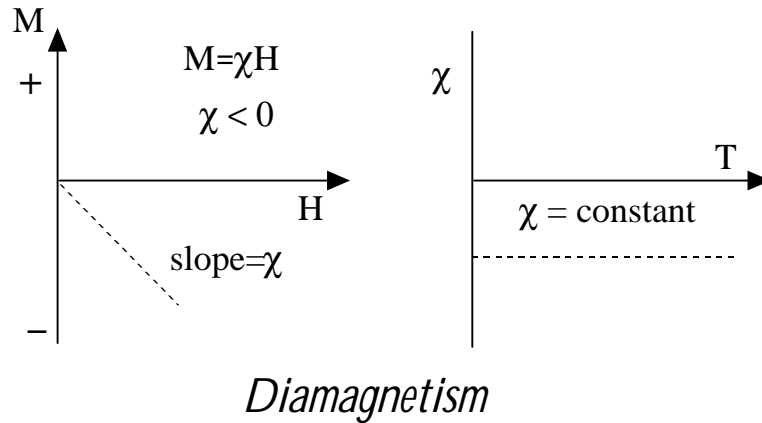
The magnetic behavior of materials can be classified into the following five major groups:

1. Diamagnetism
2. Paramagnetism
3. Ferromagnetism
4. Antiferromagnetism
5. Ferrimagnetism

Materials in the first two groups are those that exhibit no collective magnetic interactions and are not magnetically ordered. Materials in the last three groups exhibit long-range magnetic order below a certain critical temperature. Ferromagnetic and ferrimagnetic materials are usually what we consider as being magnetic (ie., behaving like iron). The remaining three are so weakly magnetic that they are usually thought of as "nonmagnetic".

1. Diamagnetism

Diamagnetism is a fundamental property of all matter, although it is usually very weak. It is due to the non-cooperative behavior of orbiting electrons when exposed to an applied magnetic field. Diamagnetic substances are composed of atoms which have no net magnetic moments (ie., all the orbital shells are filled and there are no unpaired electrons). However, when exposed to a field, a negative magnetization is produced and thus the susceptibility is negative. If we plot M vs H , we see:

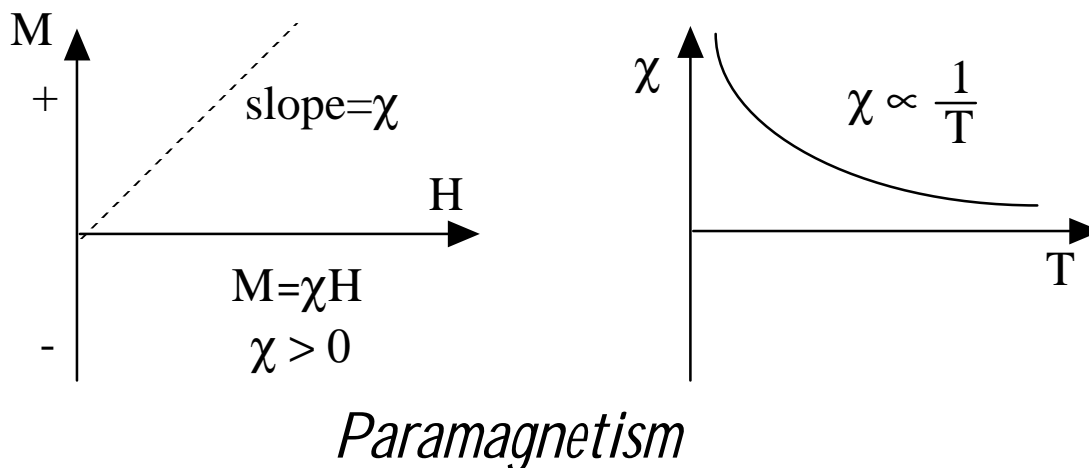


Note that when the field is zero the magnetization is zero. The other characteristic behavior of diamagnetic materials is that the susceptibility is temperature independent. Some well known diamagnetic substances, in units of $10^{-8} \text{ m}^3\text{kg}^{-1}$, include:

quartz (SiO_2)	-0.62
Calcite (CaCO_3)	-0.48
water	-0.90

2. Paramagnetism

This class of materials, some of the atoms or ions in the material have a net magnetic moment due to unpaired electrons in partially filled orbitals. One of the most important atoms with unpaired electrons is iron. However, the individual magnetic moments do not interact magnetically, and like diamagnetism, the magnetization is zero when the field is removed. In the presence of a field, there is now a partial alignment of the atomic magnetic moments in the direction of the field, resulting in a net positive magnetization and positive susceptibility.



In addition, the efficiency of the field in aligning the moments is opposed by the randomizing effects of temperature. This results in a temperature dependent susceptibility, known as the Curie Law.

At normal temperatures and in moderate fields, the paramagnetic susceptibility is small (but larger than the diamagnetic contribution). Unless the temperature is very low ($\ll 100$ K) or the field is very high paramagnetic susceptibility is independent of the applied field. Under these conditions, paramagnetic susceptibility is proportional to the total iron content. Many iron bearing minerals are paramagnetic at room temperature. Some examples, in units of $10^{-8} \text{ m}^3\text{kg}^{-1}$ include:

Montmorillonite (clay)	13
Nontronite (Fe-rich clay)	65
Biotite (silicate)	79
Siderite(carbonate)	100
Pyrite (sulfide)	30

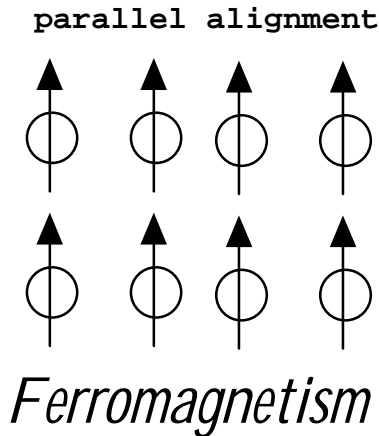
The paramagnetism of the matrix minerals in natural samples can be significant if the concentration of magnetite is very small. In this case, a paramagnetic correction may be needed.

3. Ferromagnetism

When you think of magnetic materials, you probably think of iron, nickel or magnetite. Unlike paramagnetic materials, the atomic moments in these materials exhibit very strong interactions. These interactions are produced by electronic exchange forces and result in a parallel or antiparallel alignment of atomic moments. Exchange forces are very large, equivalent to a field on the order of 1000 Tesla, or approximately a 100 million times the strength of the earth's field.

The exchange force is a quantum mechanical phenomenon due to the relative orientation of the spins of two electron.

Ferromagnetic materials exhibit parallel alignment of moments resulting in large net magnetization even in the absence of a magnetic field.



The elements Fe, Ni, and Co and many of their alloys are typical ferromagnetic materials.

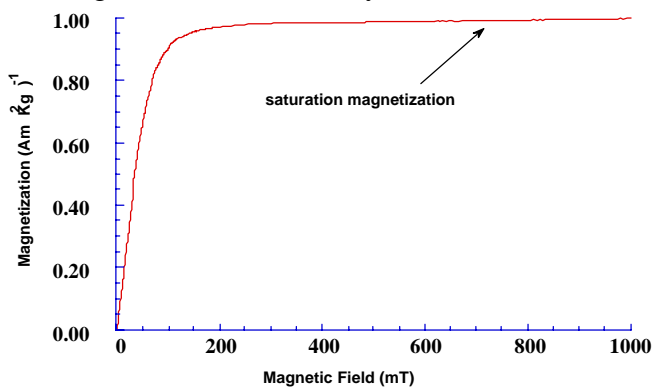
Two distinct characteristics of ferromagnetic materials are their

- (1) spontaneous magnetization and the existence of
- (2) magnetic ordering temperature

Spontaneous Magnetization

The spontaneous magnetization is the net magnetization that exists inside a uniformly magnetized microscopic volume in the absence of a field. The magnitude of this magnetization, at 0 K, is dependent on the spin magnetic moments of electrons.

A related term is the saturation magnetization which we can measure in the laboratory. The saturation magnetization is the maximum induced magnetic moment that can be obtained in a magnetic field (H_{sat}); beyond this field no further increase in magnetization occurs.



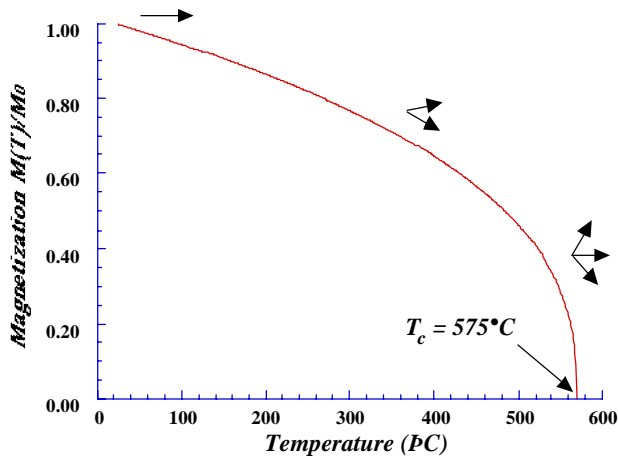
The difference between spontaneous magnetization and the saturation magnetization has to do with magnetic domains (more about domains later). Saturation magnetization is an intrinsic property, independent of particle size but dependent on temperature.

There is a big difference between paramagnetic and ferromagnetic susceptibility. As compared to paramagnetic materials, the magnetization in ferromagnetic materials is saturated in moderate magnetic fields and at high (room-temperature) temperatures:

	H_{sat} (Tesla)	T-range (K)		$\chi(10^{-8}\text{m}^3\text{kg}^{-1})$
paramagnets:	>10	<<100	50	
ferromagnets:	1	300		1000-10000

Curie Temperature

Even though electronic exchange forces in ferromagnets are very large, thermal energy eventually overcomes the exchange and produces a randomizing effect. This occurs at a particular temperature called the Curie temperature (T_C). Below the Curie temperature, the ferromagnet is ordered and above it, disordered. The saturation magnetization goes to zero at the Curie temperature. A typical plot of magnetization vs temperature for magnetite is shown below.

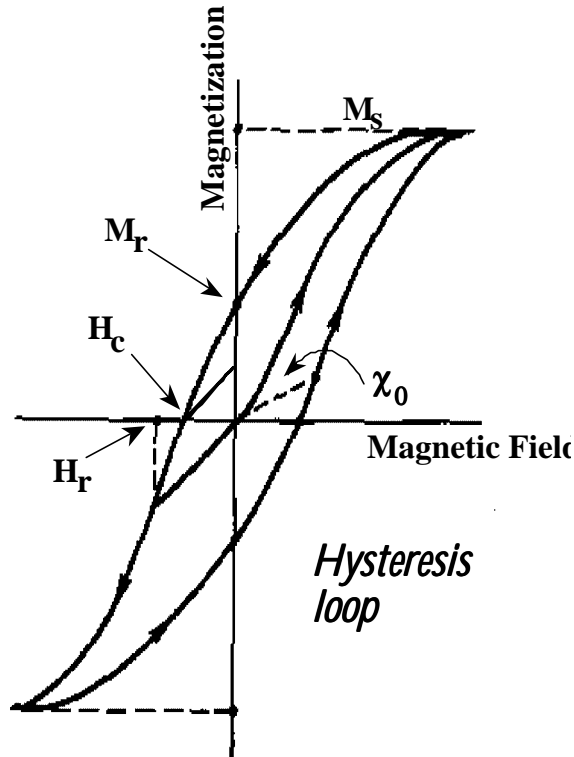


Because we are still dealing with atoms having magnetic moments, a ferromagnet above the Curie temperature is paramagnetic.

The Curie temperature is also an intrinsic property and is a diagnostic parameter that can be used for mineral identification. However, it is not foolproof because different magnetic minerals, in principle, can have the same Curie temperature.

Hysteresis

In addition to the Curie temperature and saturation magnetization, ferromagnets can retain a memory of an applied field once it is removed. This behavior is called hysteresis and a plot of the variation of magnetization with magnetic field is called a hysteresis loop.



The **saturation magnetization** (M_s) is measured in the laboratory by applying a magnetic field of 1-2 Tesla. This field strength is usually sufficient to saturate most magnetic minerals. Upon reducing the field to zero, the magnetization does not go to zero but persists as a **saturation remanence** (M_r). Increasing the field in the

negative direction, a point is reached where the induced magnetization becomes zero. The field at this point is called the **coercivity** (H_c). Increasing the field further in the negative direction results in saturation again but in the negative direction.

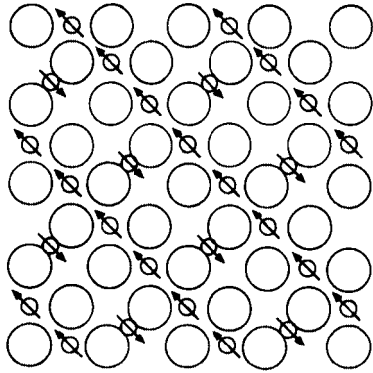
Another hysteresis property is the **coercivity of remanence** (H_r). This is the reverse field which, when applied and then removed, reduces the saturation remanence to zero. It is always larger than the coercive force.

The **initial susceptibility** (χ_0) is the magnetization observed in low fields, on the order of the earth's field (50-100 μT).

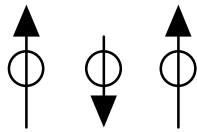
The various hysteresis parameters are not solely intrinsic properties but are dependent on grain size, domain state, stresses, and temperature. Because hysteresis parameters are dependent on grain size, they are useful for magnetic grain sizing of natural samples.

4. Ferrimagnetism

In ionic compounds, such as oxides, more complex forms of magnetic ordering can occur as a result of the crystal structure. One type of magnetic ordering is called ferrimagnetism. A simple representation of the magnetic spins in a ferrimagnetic oxide is shown here.



Ferrimagnetism



spontaneous magnetization, Curie temperatures, hysteresis, and remanence. However, ferro- and ferrimagnets have very different magnetic ordering.

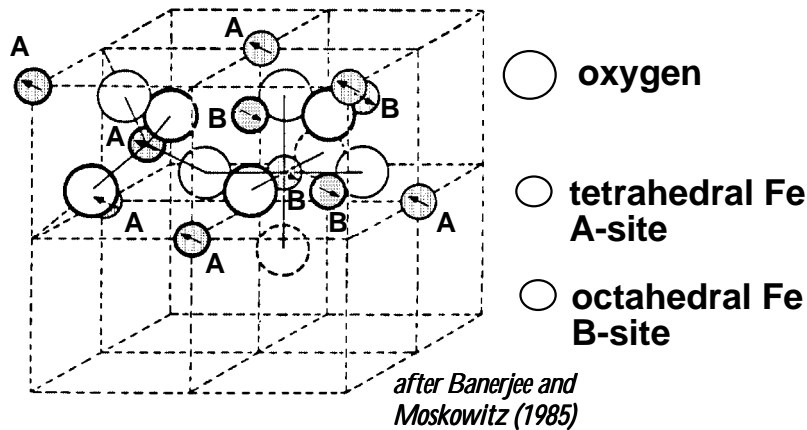
Magnetite is a well known ferrimagnetic material. Indeed, magnetite was considered a ferromagnet until Néel in the 1940's, provided the theoretical framework for understanding ferrimagnetism.

Crystal Structure of Magnetite

Let's take a closer look at the crystal structure of magnetite.

The magnetic structure is composed of two magnetic sublattices (called A and B) separated by oxygens. The exchange interactions are mediated by the oxygen anions. When this happens, the interactions are called indirect or superexchange interactions. The strongest superexchange interactions result in an antiparallel alignment of spins between the A and B sublattice.

In ferrimagnets, the magnetic moments of the A and B sublattices are not equal and result in a net magnetic moment. Ferrimagnetism is therefore similar to ferromagnetism. It exhibits all the hallmarks of ferromagnetic behavior-

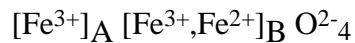


Magnetite, Fe_3O_4 crystallizes with the spinel structure. The large oxygen ions are close packed in a cubic arrangement and the smaller Fe ions fill in the gaps. The gaps come in two flavors:

tetrahedral site: Fe ion is surrounded by four oxygens
 octahedral site: Fe ion is surrounded by six oxygens

The tetrahedral and octahedral sites form the two magnetic sublattices, A and B respectively. The spins on the A sublattice are antiparallel to those on the B sublattice. The two crystal sites are very different and result in complex forms of exchange interactions of the iron ions between and within the two types of sites.

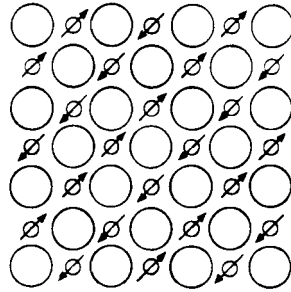
The structural formula for magnetite is



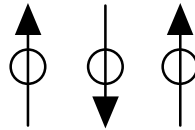
This particular arrangement of cations on the A and B sublattice is called an inverse spinel structure. With negative AB exchange interactions, the net magnetic moment of magnetite is due to the B-site Fe^{2+} .

5. Antiferromagnetism

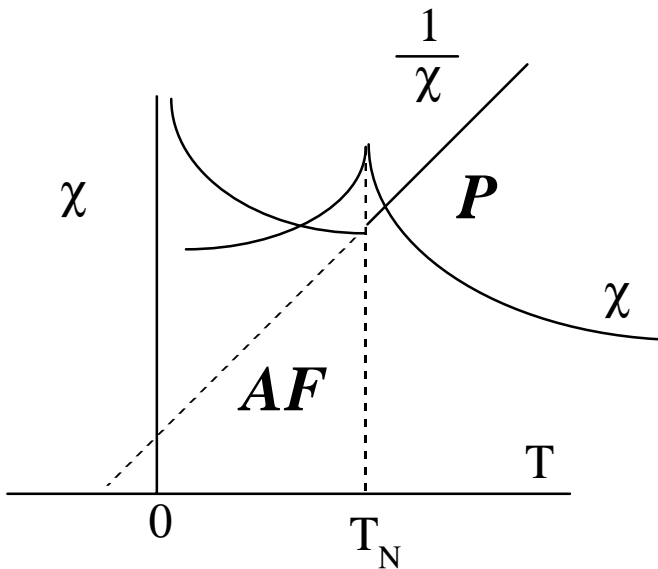
If the A and B sublattice moments are exactly equal but opposite, the net moment is zero. This type of magnetic ordering is called antiferromagnetism.



Antiferromagnetism

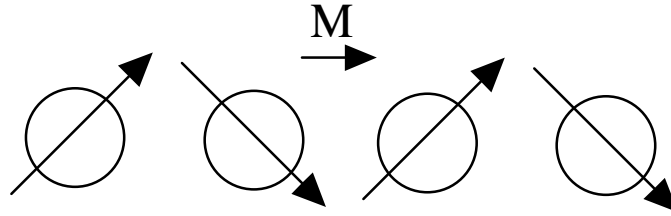


Antiferromagnetic materials also have zero remanence, no hysteresis, but a small positive susceptibility that varies in a peculiar way with temperature.



The clue to antiferromagnetism is the behavior of susceptibility above a critical temperature, called the Néel temperature (T_N). Above T_N , the susceptibility obeys the Curie-Weiss law for paramagnets but with a negative intercept indicating negative exchange interactions.

Slight deviations from ideal antiferromagnetism can exist if the anti-parallelism is not exact. If neighboring spins are slightly tilted ($<1^\circ$) or canted, a very small net magnetization can be produced.



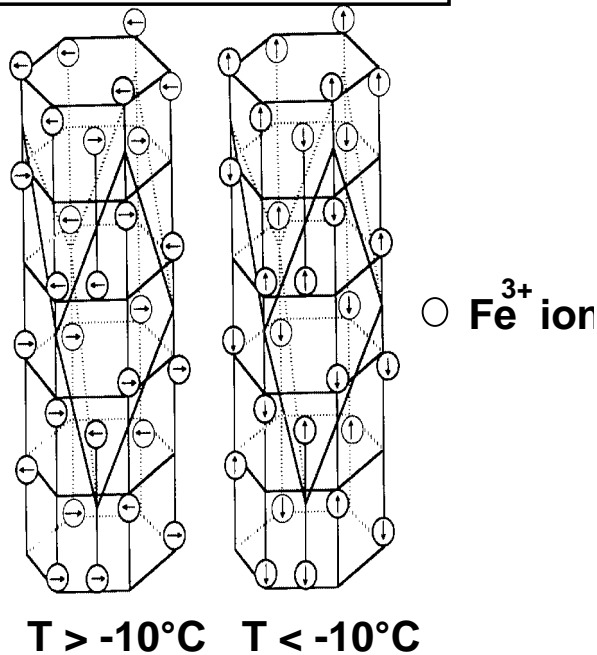
Canted Antiferromagnetism

This is called canted antiferromagnetism and hematite is a well known example. Canted antiferromagnets exhibit many of the typical magnetic characteristics of ferro- and ferrimagnets (e.g., hysteresis, remanence, Curie temperature).

Crystal Structure of Hematite

Hematite crystallizes in the corundum structure with oxygen ions in an hexagonal close packed framework. The magnetic moments of the Fe^{3+} ions are ferromagnetically coupled within specific c-planes, but antiferromagnetically coupled between the planes.

Crystal Structure of Hematite

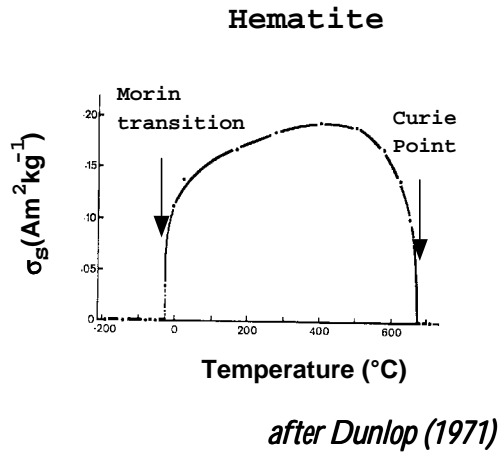


after Fuller (1987)

Above -10°C , the spin moments lie in the c-plan but are slightly canted. This produces a weak spontaneous magnetization within the c-plan ($\sigma_s = 0.4 \text{ Am}^2/\text{kg}$).

Below -10°C , the direction of the antiferromagnetism changes and becomes parallel to the c-axis; there is no spin canting and hematite becomes a perfect antiferromagnet.

The spin-flop transition is called the Morin transition.



Magnetic Properties of Minerals

Mineral	Composition	Magnetic Order	$T_C(^{\circ}\text{C})$	$\sigma_s (\text{Am}^2/\text{kg})$
Oxides				
Magnetite	Fe_3O_4	ferrimagnetic	575-585	90-92
Ulvospinel	Fe_2TiO_2	AFM	-153	
Hematite	$\alpha\text{Fe}_2\text{O}_3$	canted AFM	675	0.4
Ilmenite	FeTiO_2	AFM	-233	
Maghemite	$\gamma\text{Fe}_2\text{O}_3$	ferrimagnetic	~ 600	~ 80
Jacobsite	MnFe_2O_4	ferrimagnetic	300	77
Trevorite	NiFe_2O_4	ferrimagnetic	585	51
Magnesioferrite	MgFe_2O_4	ferrimagnetic	440	21

Sulfides

Pyrrhotite	Fe ₇ S ₈	ferrimagnetic	320	20
Greigite	Fe ₃ S ₄	ferrimagnetic	~333	~25
Troilite	FeS	AFM	305	

Oxyhydroxides

Goethite	αFeOOH	AFM, weak FM	~120	<1
lepidocrocite	γFeOOH	AFM(?)	-196	
feroxyhyte	δFeOOH	ferrimagnetic	~180	<10

Metals & Alloys

Iron	Fe	FM	770	218
Nickel	Ni	FM	358	55
Cobalt	Co	FM	1131	161
Awaruite	Ni ₃ Fe	FM	620	120
Wairauite	CoFe	FM	986	235

FM ferromagnetic order

AFM antiferromagnetic order

T_c Curie or Néel Temperature

σ_s saturation magnetization at room-temperature

Magnetic Anisotropy

The theory of ferro- and ferrimagnetism is based on electronic exchange forces. These forces are so strong that these material are spontaneously magnetized, even in the absence of an applied field. Yet, in the laboratory we need to apply magnetic fields to saturate a ferro- or ferrimagnetic material. In some cases, the material in bulk form has a remanence of nearly zero. This raises the question:

Why aren't all ferro- and ferrimagnetic materials magnetized to their saturated states, even in zero field?

To answer this question, it was postulated back in 1907, when the theory of ferromagnetism was first advanced, that ferromagnets are subdivided into many small subvolumes, called domains. Each domain is spontaneously magnetized to saturation, but the direction of magnetization varies from domain to domain. The net vector sum of all the

domains therefore produce a total magnetization of near zero. It wasn't until the 1930's that domains were experimentally confirmed.

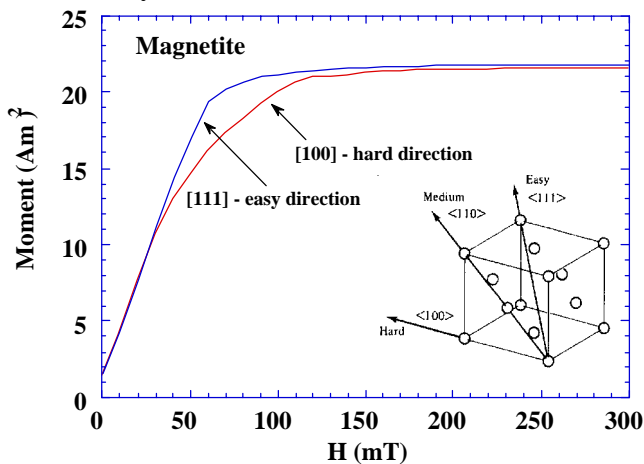
Before we study domains, we need to know a few facts about the influence of the crystal structure and the shape of grains on the direction of magnetization. The dependence of magnetic properties on a preferred direction is called magnetic anisotropy. There are several different types of anisotropy:

<u>Type</u>	<u>depends on</u>
1. magnetocrystalline-	crystal structure
2. shape-	grain shape
3. stress-	applied or residual stresses

Magnetic anisotropy strongly affects the shape of hysteresis loops and controls the coercivity and remanence. Anisotropy is also of considerable practical importance because it is exploited in the design of most magnetic materials of commercial importance.

Magnetocrystalline Anisotropy

Magnetocrystalline anisotropy is an intrinsic property of a ferrimagnet, independent of grain size and shape. It can be most easily seen by measuring magnetization curves along different crystal directions.



For example, here are magnetization curves for magnetite.

Depending on the crystallographic orientation of the sample in the magnetic field, the magnetization reaches saturation in different fields.

In magnetite, above 130 K,

- <111> is the easy direction of magnetization
- <100> is the hard direction of magnetization
- <110> is the intermediate direction of magnetization.

For a sphere of magnetite there will be six easy directions of magnetization corresponding to the three [111] axes.

Magnetocrystalline anisotropy is the energy necessary to deflect the magnetic moment in a single crystal from the easy to the hard direction. The easy and hard directions arise from the interaction of the spin magnetic moment with the crystal lattice (spin-orbit coupling).

In cubic crystals, like magnetite, the magnetocrystalline anisotropy energy is given by a series expansion in terms of the angles between the direction of magnetization and the cube axes. It is sufficient to represent the anisotropy energy in an arbitrary direction by just the first two terms in the series expansion. These two terms each have an empirical constant associated with them called the first- and second order anisotropy constants, or K_1 and K_2 , respectively.

At 300 K,

$$K_1 = -1.35 \times 10^5 \text{ ergs/cm}^3$$

$$K_2 = -0.44 \times 10^5 \text{ ergs/cm}^3.$$

In hexagonal crystals, like hematite, the weak ferromagnetism lies in the basal plane, which is an easy plane of magnetization. The c-axis is the hard direction. It is extremely difficult to flip the magnetization out of the basal plan into the direction of the c-axis.

In these materials, saturation is usually never reached in fields normally used in the laboratory (1-2 Tesla). This behavior is useful to distinguish hematite from magnetite and other cubic magnetic minerals.

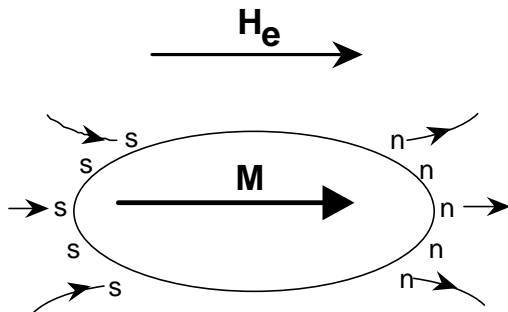
Stress Anisotropy

In addition to magnetocrystalline anisotropy, there is another effect related to spin-orbit coupling called magnetostriction. Magnetostriction arises from the strain dependence of the anisotropy constants. Upon magnetization, a previously demagnetized crystal experiences a strain that can be measured as a function of applied field along the principal crystallographic axes. A magnetic material will therefore change its dimension when magnetized.

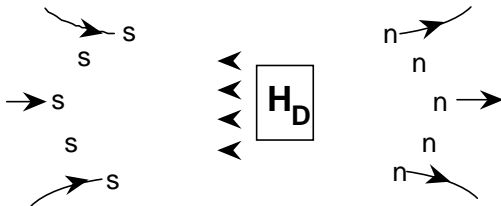
The inverse affect, or the change of magnetization with stress also occurs. A uniaxial stress can produce a unique easy axis of magnetization if the stress is sufficient to overcome all other anisotropies. The magnitude of the stress anisotropy is described by two more empirical constants known as the magnetostriction constants (λ_{111} and λ_{100}) and the level of stress.

Shape Anisotropy

The third type of anisotropy is due to the shape of a mineral grain. A magnetized body will produce magnetic charges or poles at the surface. This surface charge distribution, acting in isolation, is itself another source of a magnetic field, called the demagnetizing field. It is called the demagnetizing field because it acts in opposition to the magnetization that produces it.



Magnetization Produces Apparent Surface Pole Distribution



Demagnetizing Field Due to Apparent Surface Pole Distribution

$$H_i = H_e - H_D$$

$$H_D = NM$$

N = demagnetizing factor

usually never important.

For example, take a long thin needle shaped grain. The demagnetizing field will be less if the magnetization is along the long axis than if it is along one of the short axes. This produces an easy axis of magnetization along the long axis. A sphere, on the other hand, has no shape anisotropy. The magnitude of shape anisotropy is dependent on the saturation magnetization.

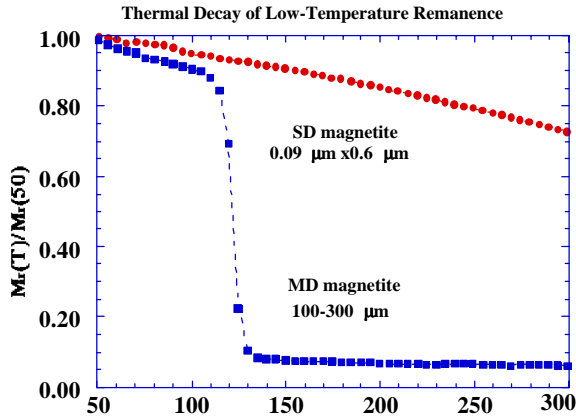
For magnetite, smaller than about 20 microns, shape anisotropy is the dominant form of anisotropy. In larger sized particles, shape anisotropy is less important than magnetocrystalline anisotropy.

For hematite, because the saturation magnetization is so low, shape anisotropy is

Temperature Dependence of Anisotropy

Both the magnetocrystalline and magnetostriction constants are dependent on temperature and, especially in magnetite, result in interesting variations of magnetization with temperature.

At room temperature, the sign of the K_1 is negative. However, at about 118K, called the isotropic point, the anisotropy constant K_1 goes through zero and becomes positive.



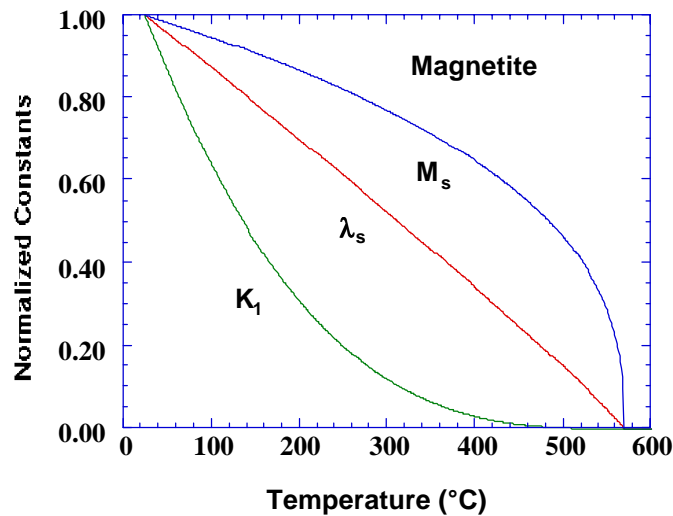
When the magnetocrystalline anisotropy vanishes, the original remanence carried by grains in which the remanence is controlled by magnetocrystalline anisotropy can be lost. This provides a simple method for distinguishing different

domain states. In grains where the remanence is controlled by shape anisotropy (ie small grains) or stress anisotropy, no remanence should be lost upon cooling through the isotropic point.

Hematite has a similar low-temperature transition at -10°C (Morin Transition). However, the cause of the transition is different. Below -10°C , hematite converts to a perfect antiferromagnet and remanence is completely lost below the transition.

Both smaller particle sizes and the presence of impurity atoms seem to suppress these transitions, particularly for hematite.

Above room temperature, the magnetocrystalline and magnetostriction constants decrease with temperature and vanish at the Curie Temperature.

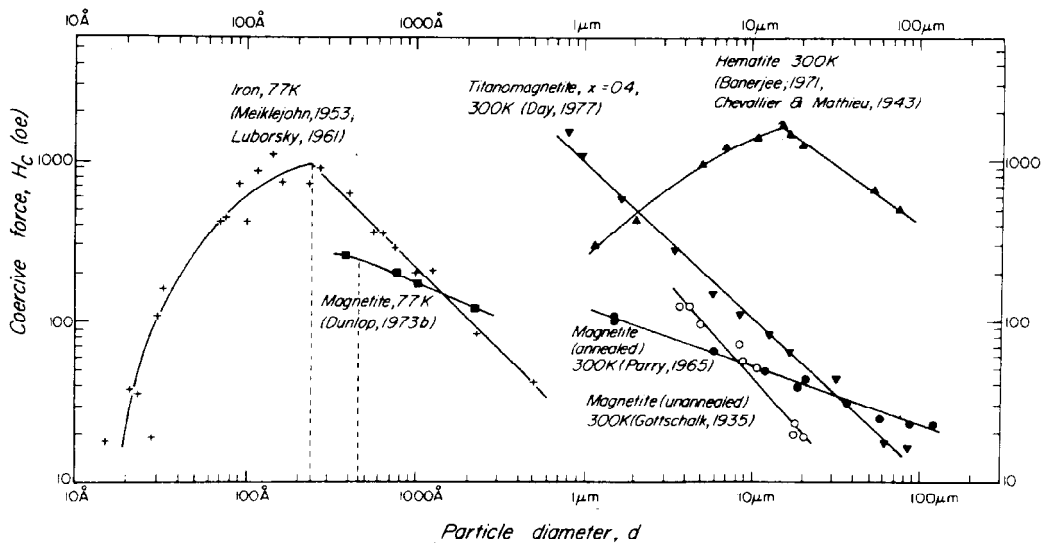


Domain Theory

A remarkable property of ferrimagnetic materials is not so much that they have a spontaneous magnetization, but rather that their magnetization can be influenced by the application of very low magnetic fields. Even the earth's field ($50 \mu\text{T}$) can cause magnetization changes even though the interatomic exchange forces responsible for the spontaneous magnetization are equivalent to a field of about 1000 T, almost 100 million times greater than the earth's field.

What allows this to occur is the fact that the sample is actually composed of small regions called magnetic domains, within each of which the local magnetization is saturated but not necessarily parallel. Domains are small (1-100's microns), but much larger than atomic distances.

The existence of domains is hinted at by the observation that some magnetic properties, and in particular, coercivity and remanence vary greatly with grain size. This is best illustrated in the figure below, which shows the variation of H_C with grain size.

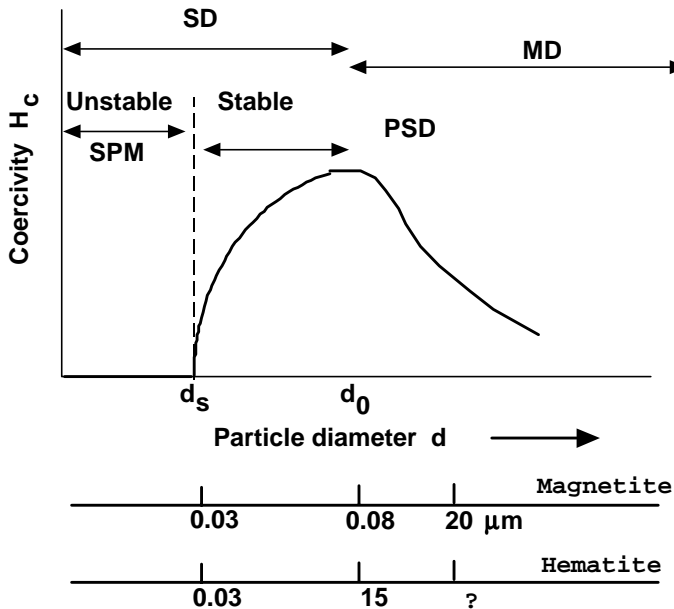


after Dunlop (1981)

T

he magnetic behavior can be subdivided on the basis of grain size into

- SPM superparamagnetic
- SD single domain
- PSD pseudo-single domain
- MD multidomain



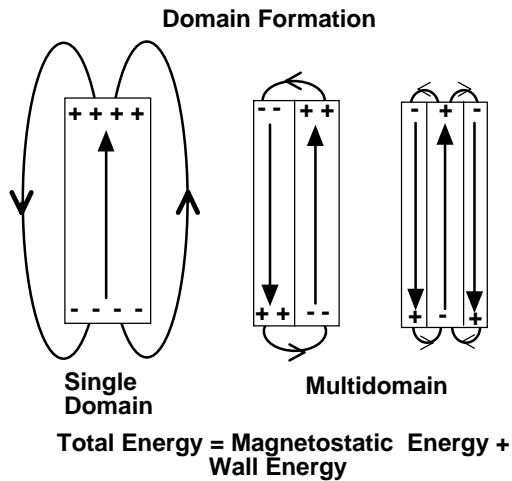
The maximum coercivity for a given material occurs within its SD range. For larger grain sizes, coercivity decreases as the grain subdivides into domains. For smaller grain sizes, coercivity again decreases, but this time due to the randomizing effects of thermal energy.

Domains constitute a fundamental concept in magnetism. A ferro- or ferrimagnetic material may be generally defined as one that possesses a spontaneous

magnetization, M_s , dependent on temperature, but only slightly dependent on applied field. The theory of ferromagnetism, based on electronic exchange forces, predicts the magnitude of M_s , but says nothing about the direction of M_s . Experimentally, it is observed that for a homogeneous specimen at constant temperature, the magnitude of M_s is uniform but the

direction of M_s is in general not uniform from one region to another (on a scale of microns to millimeters). Uniformity of direction is attained only by applying a large enough field to drive the domains out of the sample, or by reducing the particle's dimensions to small enough size to prevent domain formation.

Domains are formed for the following reason. Consider a large single crystal.

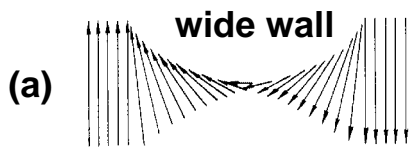


Suppose it is uniformly magnetized, and hence a single domain. Surface charges will form on the ends due to the magnetization and are themselves a second source of a magnetic field (the demagnetizing field). The energy associated with the surface charge distribution is called the magnetostatic energy. It is just the volume integral of the field over all space.

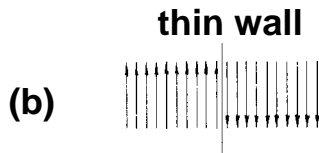
The magnetostatic energy can be approximately halved if the magnetization splits into two domains magnetized in opposite directions. This brings (+) and (-) charges closer together, thus decreasing the spatial extent of the demagnetizing field.

This subdivision into more and more domains can not continue indefinitely because the transition region between domains (called a domain wall) requires energy to be produced and maintained. Eventually an equilibrium number of domains will be reached for a given particle size.

Domain walls are interfaces between regions in which the magnetization has different directions. Within the wall, the magnetization must change direction from that in one domain to that in the other domain. Domain walls have a finite width that is determined principally by exchange and magnetocrystalline energy.



Let's consider a domain wall in which the magnetization changes by 180° . The change in magnetization within the wall can be gradual as in (a) or abrupt as in (b).



The exchange energy acts to keep spins parallel and can be kept small if the 180° rotation

takes place gradually, over many atomic units. Therefore, the exchange energy is small in (a) but large in (b).

However, the spins within the wall are no longer aligned along an easy axis of magnetization. This produces an anisotropy energy, which is high in (a) but low in (b).

The exchange energy tends to make the wall as wide as possible whereas the anisotropy tends to make the wall as thin as possible. As a result of this competition between exchange and anisotropy energies, the domain wall has a finite width (on the order of 100 nm) and surface energy.

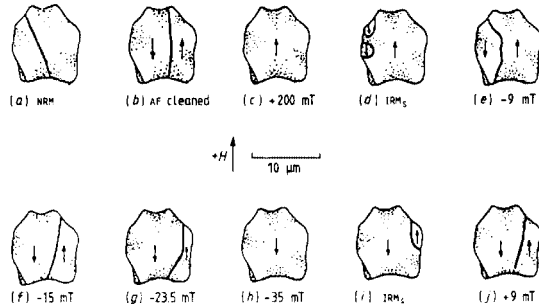
The interplay between long range and short range effects results in the domain states being grain-size dependent. In addition, the number of domains for a given grain size depends on the magnitudes of the exchange, magnetocrystalline, and saturation magnetization. As mentioned before, these constants are dependent on temperature as well as composition. Hence domain states in different magnetic minerals (magnetite and hematite) will have a different grain size dependence. The domain states will also vary with temperature for a single grain size. However, as a rule of thumb, the larger the grain size the more domains it contains.

Single Domain (SD)

As the grain size decreases, a critical size will be reached where the grain can no longer accommodate a wall. Below this critical size, the grain contains a single domain (SD). An SD grain is uniformly magnetized to its saturation magnetization.

SD grains are very important. To change the magnetization of a MD grain, all you need to do is translate the domain wall, a energetically easy process, which can be accomplished in relatively low fields. Thus MD grains are magnetically soft with low values of coercivities and remanence.

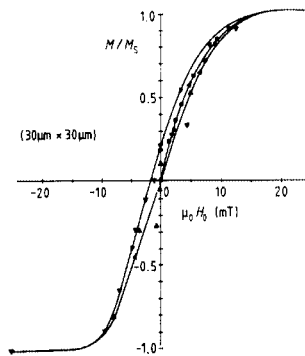
Displacement of domain walls with changing magnetic fields



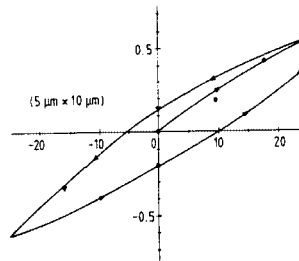
(after Halgedahl and Fuller, 1983)

However, the only way to change the magnetization of a SD grain is to rotate the magnetization, an energetically difficult process. Thus, SD grains are magnetically hard and have high coercivities and remanence. Here is an example of an SD and MD grain as characterized by hysteresis loops:

MD type



SD type

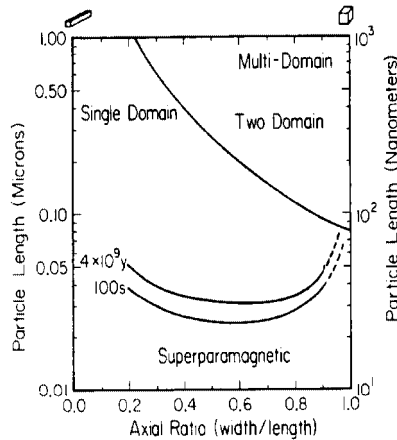


(after Dunlop (1990))

The critical size for SD behavior depends on several factors including, the saturation magnetization and the shape of the grain. Most estimates of the SD-MD transition size are

based on theoretical calculations. For magnetite, the best estimate for the transition size is about 80 nm. Here are some theoretical results:

Theoretical Domain Calcula for Magnetite



after Bulter and Banerjee (1975)

For hematite, the transition size from SD to MD is much larger (15 μm), primarily because the saturation magnetization is about 200 times lower than for magnetite.

Pseudo-Single Domain (PSD)

The distinction between SD and MD is straightforward. However, small MD grains exhibit a mixture of SD-like (high remanence) and MD-like (low coercivity) behavior. For magnetite, this behavior occurs in the size range between 0.1-20 μm .

There has been much theoretical and experimentally work on PSD grains. Some current thinking is that small MD particles that contain just a few domains may actually have difficulty nucleating domains. In some cases MD grains exist in metastable SD states. The transformation of one domain state into another, such as addition or loss of domains, is call transdomain transformation.

The importance of PSD behavior in magnetite, is that the grain size range for PSD behavior covers the range in sizes that most commonly occur in natural samples.

Superparamagnetism (SPM)

As particle size continues to decrease within the SD range, another critical threshold is reached, at which remanence and coercivity go to zero. When this happens, the grain becomes superparamagnetic.

An SD particle of volume v has a uniform magnetization directed along the easy axis of magnetization. If v is small enough, or the temperature is high enough, thermal energy (kT) will be sufficient to overcome the anisotropy energy separating the (+) and (-) magnetization states and cause a spontaneous reversal of magnetization.

For superparamagnetic particles, the net magnetic moment in zero field and at $T > 0K$, will average to zero. In an applied field, there will be a net statistical alignment of magnetic moments. This is analogous to paramagnetism, except now the magnetic moment is not that of a single atom, but to an SD particle containing 10^5 atoms. Hence, the term superparamagnetism, which denotes a much higher susceptibility value than that for simple paramagnetism.

In response to a change in the applied field or temperature, an ensemble of SPM particles will approach an equilibrium value of magnetization with a characteristic relaxation time, first derived by Néel:

$$\frac{1}{\tau} = f_0 \exp\left(\frac{-K_u v}{kT}\right)$$

where

- f_0 -frequency factor (10^9 sec^{-1})
- K_u -anisotropy constant
- v -particle volume
- k -Boltzmann constant
- T -absolute temperature

The exponential nature of the relaxation time on v and T makes it possible to define a blocking temperature, T_B (at constant volume), or blocking volume v_B , (at constant temperature) at which the magnetization goes from an unstable condition ($\tau \ll t$) to a stable condition ($\tau \gg t$). For example,

$\frac{K_u v}{kT}$	t (sec)
21	1
60	10^{17}

In spherically shaped magnetite at room-temperature, this change in energy corresponds to an increase in size from only 22 to 33 nm!

In nature, fine particles of magnetite can acquire stable remanence as they pass through the blocking conditions as they cool from high temperatures or grow authigenically or diagenetically at low temperatures.

Initial Susceptibility

Initial susceptibility is measured in a low AC or DC field (<1mT) and is defined as the ratio of M/H. Initial susceptibility is due to reversible displacements of mobile domain walls in MD particles or moment rotation in SD particles. In the latter case, low fields are not very effective in rotating SD moments. Therefore, susceptibilities in SD and PSD grains are usually lower than that of MD grains.

However, what is actually measured in the laboratory is the apparent susceptibility, χ_o , not the intrinsic susceptibility, χ_i . The difference is due to the effects of self-demagnetization.

Remember, inside a grain, the applied field, H, is modified by the demagnetizing field resulting from surface charges. The magnitude of the demagnetizing field is NM. Inside a grain, the internal field is

$$H_i = H - NM$$

$$M = \chi_i H_i$$

The observed susceptibility is the ratio of M to the applied field

$$\chi_o = \frac{M}{H} = \frac{\chi_i}{[1 + N\chi_i]}$$

For strongly magnetic materials, like magnetite

$$N\chi_i > 1$$

$$\chi_o \approx \frac{1}{N}$$

N is weakly related to grain shape and domain state. It is usually assumed to be a constant, independent of grain size. If this is so, low-field susceptibility can be used as a reliable measure of magnetite content.

A small fraction of SPM particles can contribute significantly to the room-temperature susceptibility of SD or MD grains. Calculations show SPM susceptibility can be 10-100 times that of an equivalent amount of SD grains.

Frequency Dependence of Susceptibility

Low-field susceptibility can also be measured at different frequencies of the applied AC field. SPM grains show the most pronounced frequency dependence of low-field susceptibility. Changing the measurement frequency is basically changing the amount of time allowed for the grains to react to a change in applied field. This is the same as changing the blocking

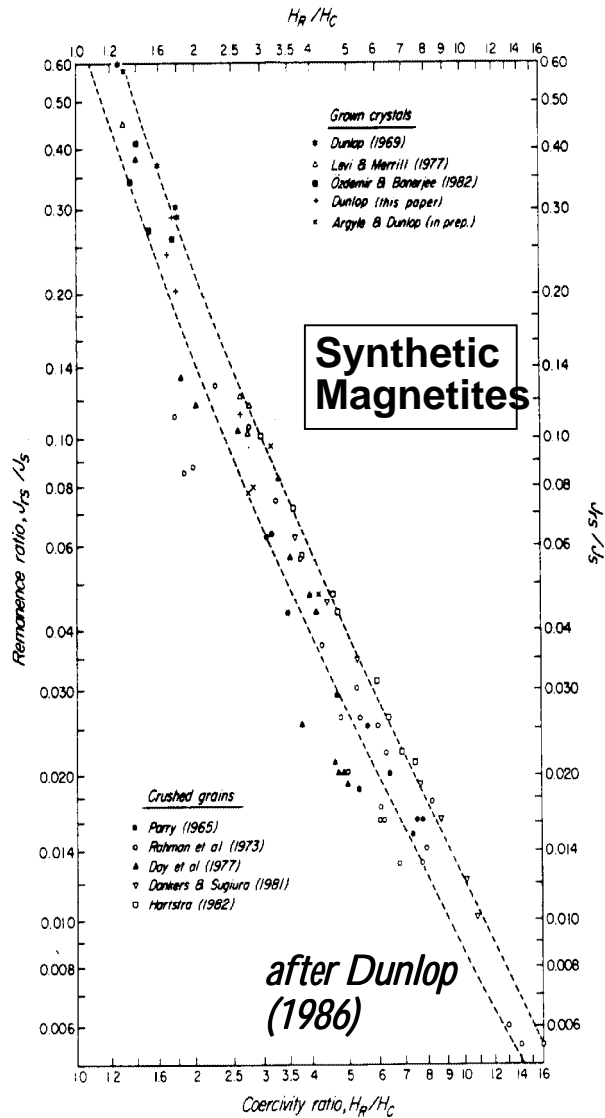
volumes. As the frequency of the measurement increases, the SPM/SD boundary shifts to smaller volumes and more grains become blocked.

Experimental results show that the % decrease in χ_0 per decade of frequency is:

1-20% SPM grains
<1% SD,MD grains

Hysteresis Properties of SD, PSD, and MD Particles

The shape of a hysteresis loop is determined partly by the domain state. Loops for SD materials are typically wider than loops for MD materials. This is just a reflection of the higher coercivity and remanence in SD material. The hysteresis loop parameters, M_r/M_s and H_r/H_c , have proven very useful in distinguishing domain state. In fact, M_r/M_s is a definitive test for differentiating between SD and non-SD particles. Here are results for magnetite:



SD Hysteresis Properties

For an assembly of SD grains with randomly oriented easy axes, M_r/M_s can be calculated and depends on the type of anisotropy:

Type of Anisotropy	M_r/M_s	Source
uniaxial	0.5	shape, stress
magnetocrystalline (cubic)		intrinsic
$K_1 < 0$	0.87	
$K_1 > 0$	0.83	

$H_C > 10-15$ mT for equidimensional particles

$H_C > 30-40$ mT for acicular particles

$H_r/H_C = 1-2$

MD and PSD Hysteresis Properties

For an assembly of MD or PSD particles, it is more difficult to calculate M_r/M_S and H_r/H_C ratios. From models based on displacements of mobile domain walls and experimental results on synthetic samples, the following values are typical:

Parameter	PSD	MD
M_r/M_S	0.1-0.5	<0.1
H_r/H_C	2-4	>4
H_C	10-15 mT	<10 mT

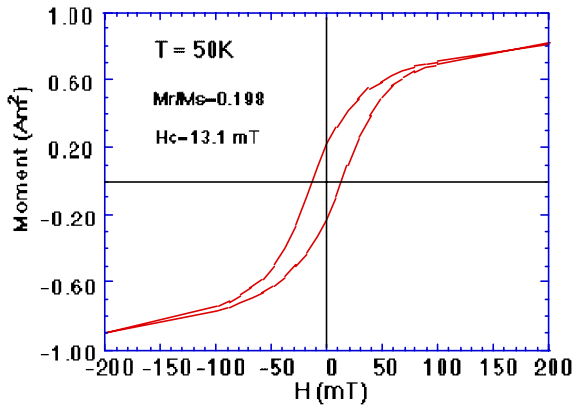
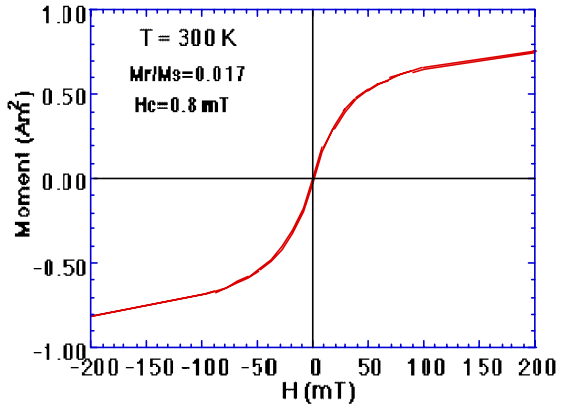
SPM Hysteresis Properties

SPM particles exhibit no remanence or coercivity. The shape of the hysteresis loop is thus extremely thin. SPM grains show a very steep initial rise in magnetization with field and then a more gradual increase to saturation. However, in a mixture of mostly SPM grains but with some SD or MD grains, typical values for hysteresis parameters are:

$$M_r/M_S \ll 0.01$$

$$H_r/H_C > 10$$

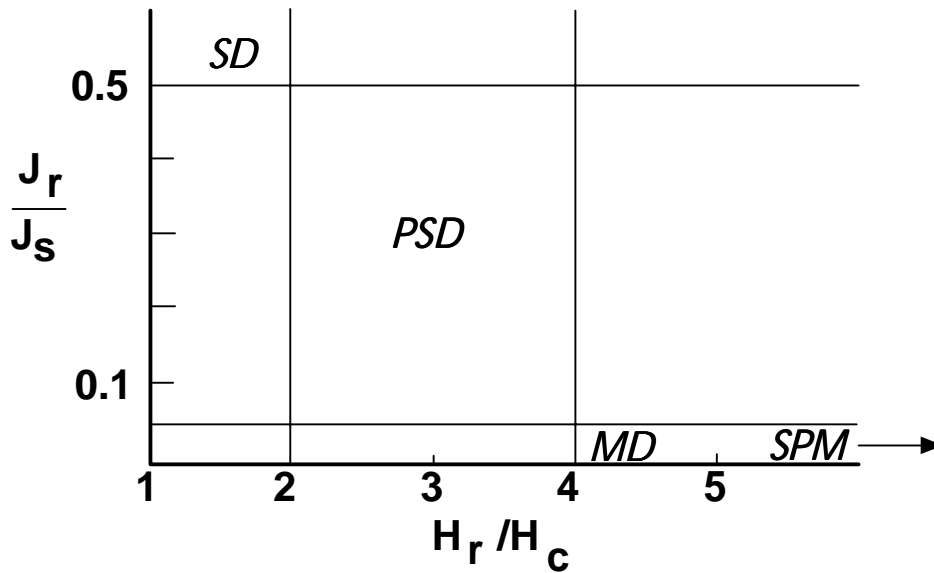
Separation of SPM from MD grains based on hysteresis properties can be a problem using just room temperature measurements. In some cases, cooling the sample down to very low temperatures can be helpful.



Grains that are SPM at room temperature can become blocked and SD at low temperatures. Significant changes in hysteresis parameters between room temperature and 77K is diagnostic of a SPM contribution.

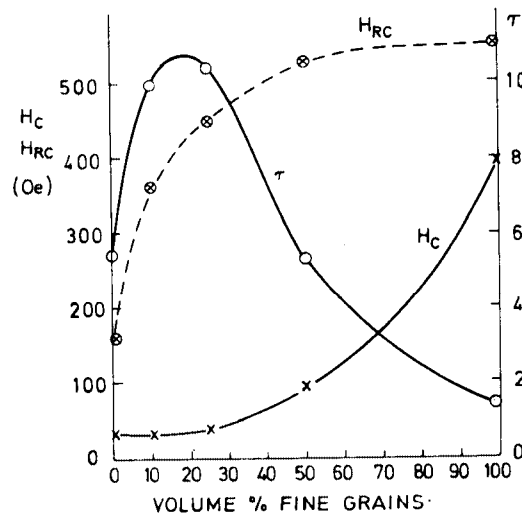
Summary

As shown above, the $M_r/M_s - H_r/H_c$ diagram is a useful indicator of domain states



Mixtures of Domain States

Often, natural samples may contain two populations of grain sizes, a coarse MD fraction and a fine SD fraction. This makes the interpretation of hysteresis data more complicated. For example, H_r/H_c is biased toward the low-coercivity fraction, as shown here



$$\tau = H_{rc} / H_c$$

after Day et al. (1977)

Very high values of this ratio indicates SPM particles.

Thermally Activated Magnetization

Néel [1949] developed a theory of remanence in SD particles based on thermal fluctuations. This model forms much of the theoretical basis for rock magnetism and provides a simple way

of looking at the effects of time, temperature and field on the magnetization and demagnetization process.

Let's consider a collection of uniformly magnetized grains with uniaxial anisotropy in a magnetic field. The magnetization of each grain has only two stable magnetic states: parallel (+) or antiparallel (-) to the field. For a large number of identical, non-interacting grains, thermally activated transitions between the two stable states will produce an average equilibrium moment

$$m_{eq} = M_s \tanh \left[\frac{vM_s h}{kT} \right]$$

Upon removal of the field, m_{eq} will decay exponentially to zero at a rate determined by a relaxation time. The relaxation time is proportional to the probability of transversing the energy barrier (E_B) produced by the uniaxial anisotropy. In the presence of an external field the relaxation time is

$$\frac{1}{\tau} = f_0 \exp \frac{-E_B}{kT} = f_0 \exp \frac{vM_s [1 - h_e/H_c]^2}{2kT}$$

where

H_c coercivity

M_s saturation magnetization

h_e external field

k Boltzmann constant

f_0 frequency constant

As stated before, grains having τ much less than a typical experimental time t will reach equilibrium from any initial magnetic state during time t and will exhibit no remanence (superparamagnetic). Grains with τ much greater than t will preserve the initial state after time t and their magnetization is effectively blocked. The blocking condition is determined at the point where $\tau = t$

$$vH_c = \frac{2kT[\ln tf_0]}{M_s} \quad : h=0$$

$$vH_c(1 - h_e/H_c)^2 = \frac{2kT[\ln tf_0]}{M_s} \quad : h \neq 0$$

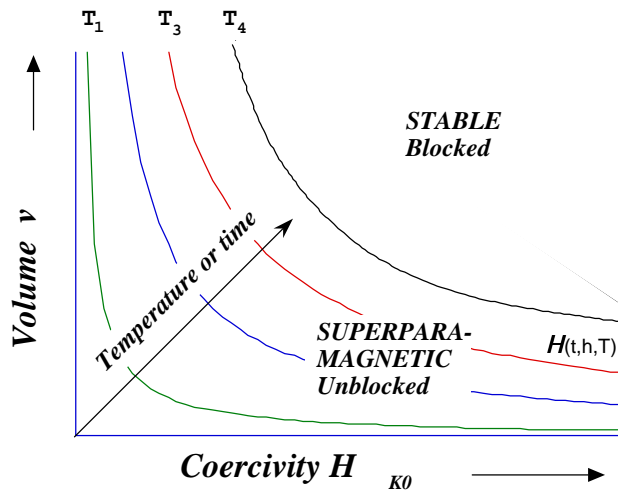
The blocking and unblocking equations can be described very succinctly on a Néel diagram. We have two cases:

case (i) $h_e=0$

The blocking equation is of the form

$$vH_c = H(t, h_e, T)$$

This equation describes an equilateral hyperbolae whose asymptotes are the v and H_c axes.



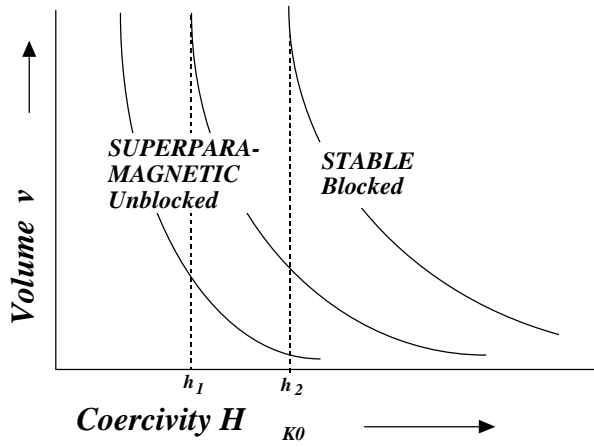
All points to the left of any curve $H(t, h_e, T)$ correspond to grains with $\tau < t$. Likewise, all points to the right have $\tau > t$.

Grains with small v and H_c will be superparamagnetic. As temperature, or time, is increased, more and more grains with larger v and H_c will become progressively unblocked, until at $T = T_B$ when

all grains become unblocked.

case (ii) $h_e = 0$

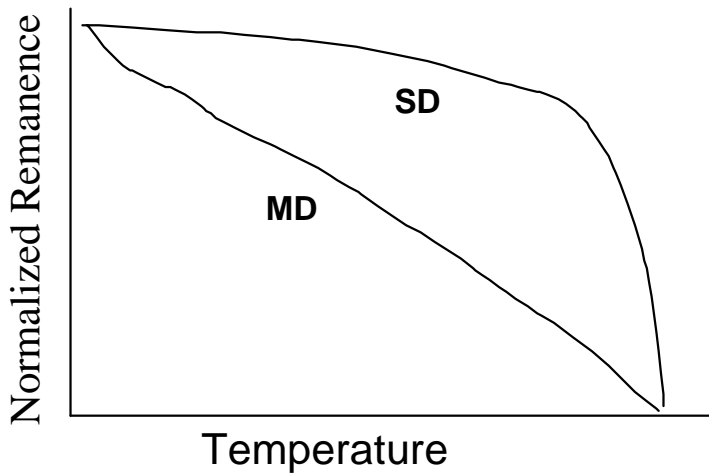
When the field is not zero, the $H(t, h_e, T)$ curves are asymptotic to the particular value of h_e



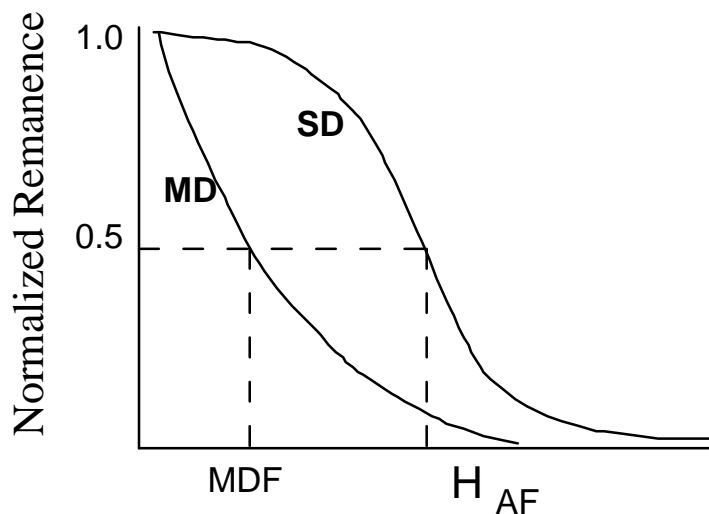
The motion of the blocking curves under the influence of h do not reproduce the motion due to temperature or time. Particles of small v and large H_c may require very large fields to become unblocked. However, the same grains can be unblocked by mild heating.

Demagnetization techniques

The above two cases of the Néel diagram provide the basis for selective demagnetization or magnetic "cleaning". The purpose of demagnetization is to remove the components of magnetization with short relaxation times which may contribute to secondary magnetizations that obscure the primary signal. Demagnetization is also useful for characterizing the coercivity distribution. There are two main methods:



Thermal Demagnetization- A sample is heated and cooled in zero field for a series of increasing temperatures. After each step the remaining remanence is measured at room-temperature. Only those grains with blocking temperatures below the demagnetization temperature will be demagnetized.



Alternating Field (AF) demagnetization- A sample is subjected to alternating field that is smoothly reduced to zero from some peak value. The AF demagnetization curve is measured by exposing the sample to a series of increasing AF peak values (5,10,15,20 ...100 mT). After each step the remaining remanence is measured. Remanence in grains with low coercivities are eased first. Remanence carried by grains

with higher coercivities remains unaltered.

The AF value needed to reduce the initial remanence by one half is called the median destructive field, or MDF

Types of Remanence

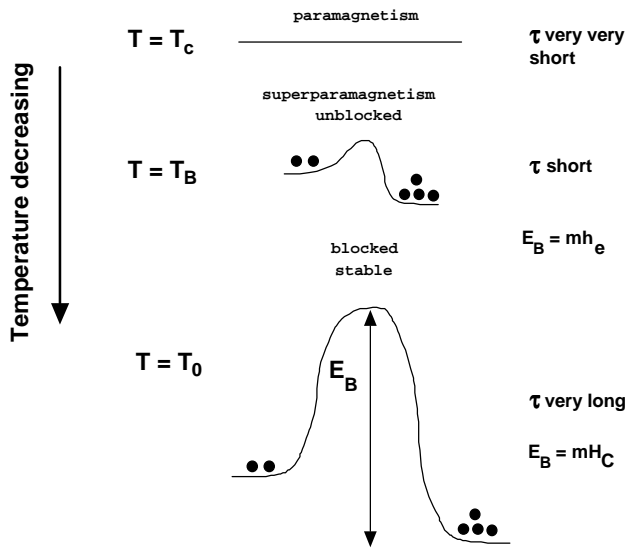
A rock carries a natural remanent magnetization (NRM) that is the vector sum of all the different possible components of magnetization acquired over its history. SD, PSD, and MD grains may all contribute to this signal. After initially acquiring a primary magnetization, grains with low relaxation times may be susceptible to remagnetization by time, temperature or chemical changes and produce secondary components of magnetization.

There are many different ways for a particle to become magnetized. The most common ones are:

Remanence	Acronym	Magnetization Process
Thermoremanent Magnetization	TRM	Magnetization acquired during cooling from temperature above the Curie Temperature in an external field
Chemical Remanent Magnetization	CRM	Magnetization acquired during chemical change in an external field
Viscous Remanent Magnetization	VRM	Magnetization acquired over time in an external field
Isothermal Remanent Magnetization	IRM	Magnetization acquired instantaneously in an external field
Anhyseretic Remanent Magnetization	ARM	Magnetization acquired by the combined effect of a large alternating field and a small DC field
Depositional Remanent Magnetization	DRM	Magnetization acquired by sediments when grains settle out of water in an external field
Post Depositional Remanent Magnetization	pDRM	Magnetization acquired after deposition due to mechanical effects in wet sediment

TRM

The energy levels of the (+) and (-) states of SD particles split in the presence of a external field producing an asymmetrical energy barrier. Moments parallel to the field have a lower energy than moments in the opposite direction. As a consequence, the number of particles in the field direction will be greater than the number in the opposite direction. This results in a net moment in the field direction.



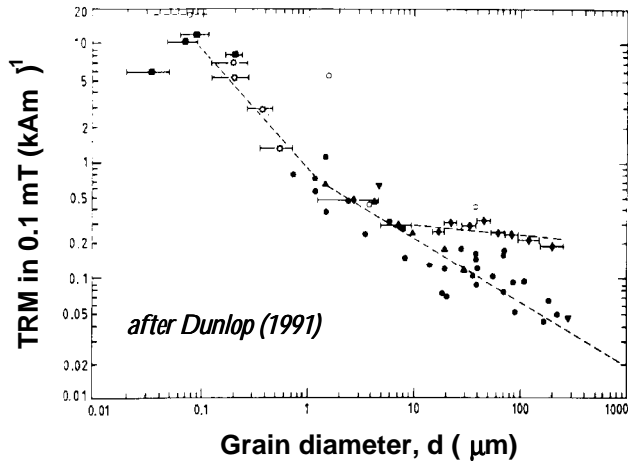
Schematic View of TRM Blocking in SD Grain

At room temperature, the energy barrier is now much higher. An external field equal to the coercivity is needed to reverse the magnetization. A weak-field, like the earth's field, which induced the TRM at high temperature has little effect on the magnetization at room temperature. The relaxation time is very long and hence the TRM is essentially stable on a geological time scale.

Just above the blocking temperature, T_B , the energy barrier is small and a weak-field can produce a net alignment of grain moments parallel to the external field. On cooling below T_B , the energy barrier becomes so large that the net alignment is preserved.

At room temperature, the energy barrier is now much higher. An external field equal to the

Grain-Size Dependence of weak-field
TRM intensity in magnetite



The intensity of a weak-field TRM is linear in applied field ($h < 1$ mT) and it is grain-size dependent:

CRM

Any type of chemical alteration may induce a magnetization:

- low-temperature oxidation
- exsolution
- diagenesis
- dehydration

There are two main types of CRM:

1. pure growth CRM from the growth of new minerals through a critical volume
2. recrystallization CRM from the recrystallization or alteration of pre-existing mineral grains.

The acquisition of CRM in (1) is similar to the process of TRM, but instead of talking about a blocking temperature, we have a blocking volume. In this case, grains grow from the superparamagnetic to the stable single domain size.

The acquisition of CRM in (2) is a more complex process because the new recrystallized phase can be influenced by the parent phase as well as the external field.

IRM

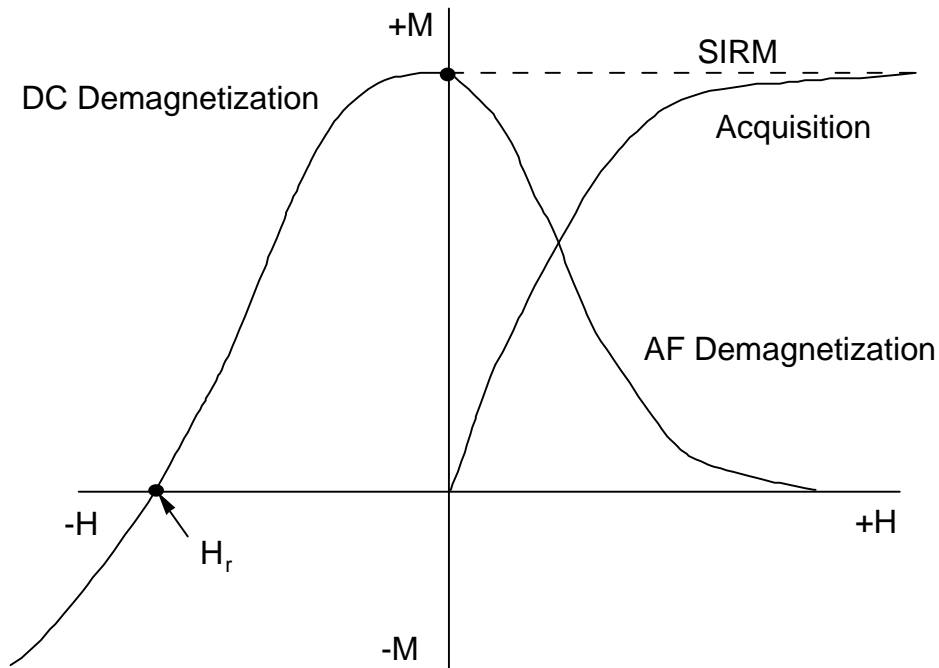
Isothermal remanent magnetization is the remanence left in the sample after a steady field (1-1000 mT) has been applied for a short time (100 sec) and then switched off.

For magnetite, in fields below approximately 50 mT, IRM is produced by irreversible domain wall translation. In fields above approximately 50 mT, IRM is produced by irreversible domain rotation in MD grains or moment rotation in SD grains.

There are three techniques used to characterize IRM:

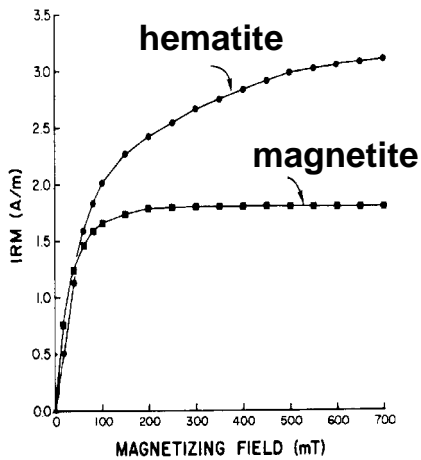
1. Acquisition measured by applying incrementally increasing fields to initially demagnetized samples. The maximum remanence is the saturation remanence.

2. DC demagnetization measured by applying incrementally increasing negative DC fields to an SIRM. The field required to reduce the SIRM to zero is the coercivity or remanence (H_r).
3. AF demagnetization measured by applying incrementally increasing alternating fields to an SIRM



IRM acquisition is a useful technique to distinguish between magnetite and hematite.

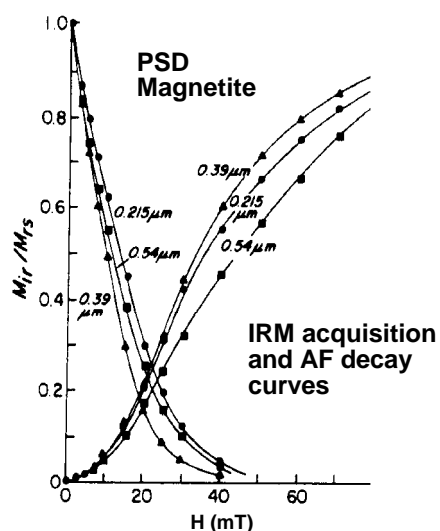
IRM Acquisition Curve



Coercivity in hematite is usually much larger than that observed in magnetite. Hence, during IRM acquisition, it is more difficult to saturate hematite than magnetite. Magnetite is typically saturated by 300-500 mT.

after Bulter (1982)

IRM acquisition and demagnetization curves are also useful for studying the effects of interactions between magnetic particles.



after Argyle and Dunlop (1990)

Non-interacting SD grains produce symmetrical curves.

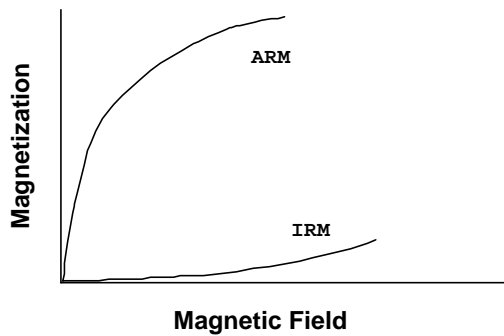
Interacting SD or MD grains produce asymmetrical curves.

ARM

Anhyseretic remanent magnetization is produced by the combined actions of a large AF and a smaller constant DC field. An ARM is imparted by slowly reducing a peak AF to zero while at the same time applying a constant DC field. ARM is a useful laboratory technique for characterizing magnetic particles.

The intensity of ARM for weak-fields (< 10 mT) is always much larger than a comparable IRM given in the same DC field.

Weak-Field ARM and IRM



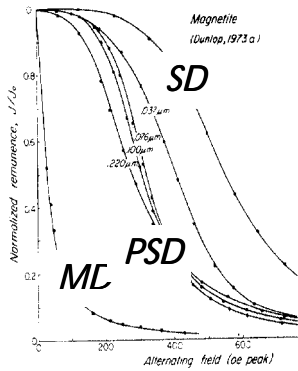
During ARM acquisition, the DC field is assisted by the AF in the acquisition process. Likewise, the remanence coercivity fractions activated by the ARM and IRM processes will also be dissimilar.

There is a similarity between ARM and TRM. The randomizing effects of the AF for ARM plays a similar role to the randomizing effects of temperature for TRM. Because of this similarity, ARM has been used as an analogue for TRM.

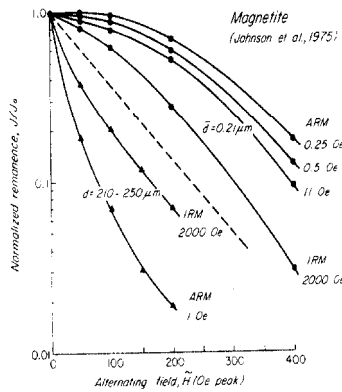
Like TRM, the intensity of ARM is linear with applied DC field for fields less than about 1 mT. The slope of this line is referred to as the ARM susceptibility.

AF Demagnetization Curves

Comparison of AF demagnetization curves of a weak-field ARM (or TRM) and a strong-field IRM has some diagnostic capability and is called the Lowrie-Fuller test. This test discriminates between SD/PSD and MD particles.



AF demagnetization of weak-field TRM



AF demagnetization of ARM and SIRM

$$\text{SD/PSD} \quad \text{MDF}_{\text{ARM}} > \text{MDF}_{\text{SIRM}}$$

$$\text{MD} \quad \text{MDF}_{\text{ARM}} < \text{MDF}_{\text{SIRM}}$$

The grain size resolution is not that great. In magnetite the threshold size between SD/PSD type curves and MD type curves is a few microns. This test can simply establish whether a particular average grain size is larger or smaller than this threshold size.

General References: Books

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