

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. [Ferrimagnetism](#)
5. [Antiferromagnetism](#)

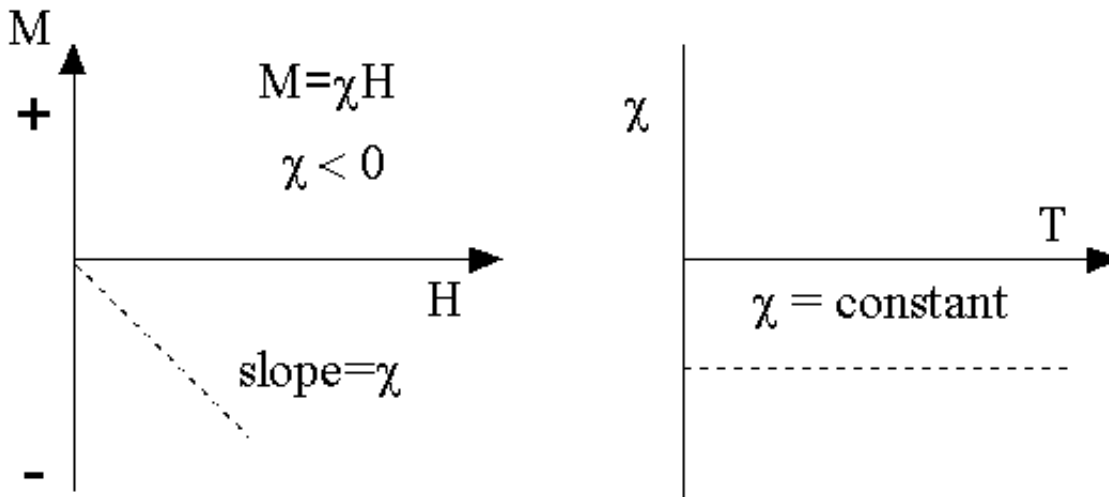
[Magnetic Properties of some common minerals](#)

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

Diamagnetism

diamagnetic substances, in units of $10^{-8} \text{ m}^3/\text{kg}$, include:

quartz (SiO_2) -0.62

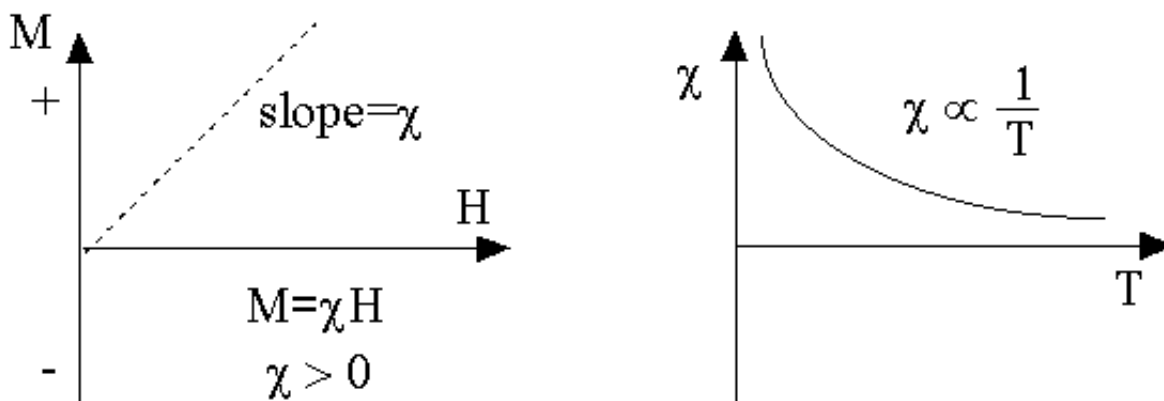
Calcite (CaCO_3) -0.48

water -0.90

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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.



Paramagnetism

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 $10^{-8} \text{ m}^3/\text{kg}$, 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.

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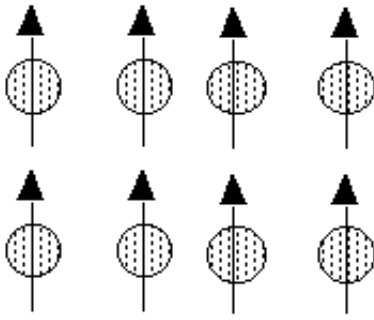
3. Ferromagnetism

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.

parallel alignment



Ferromagnetism

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

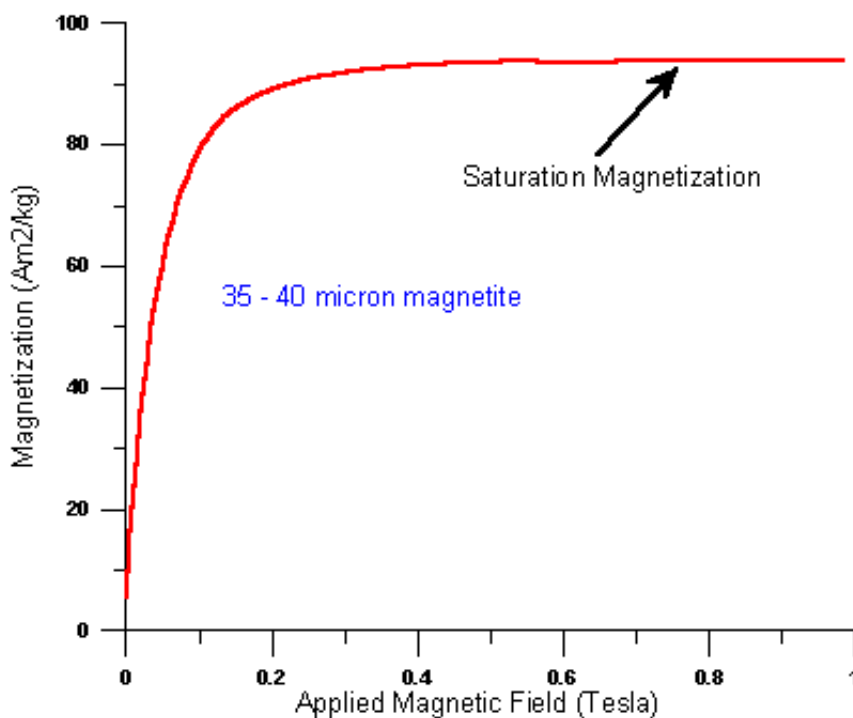
Two distinct characteristics of ferromagnetic materials are their

- (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.

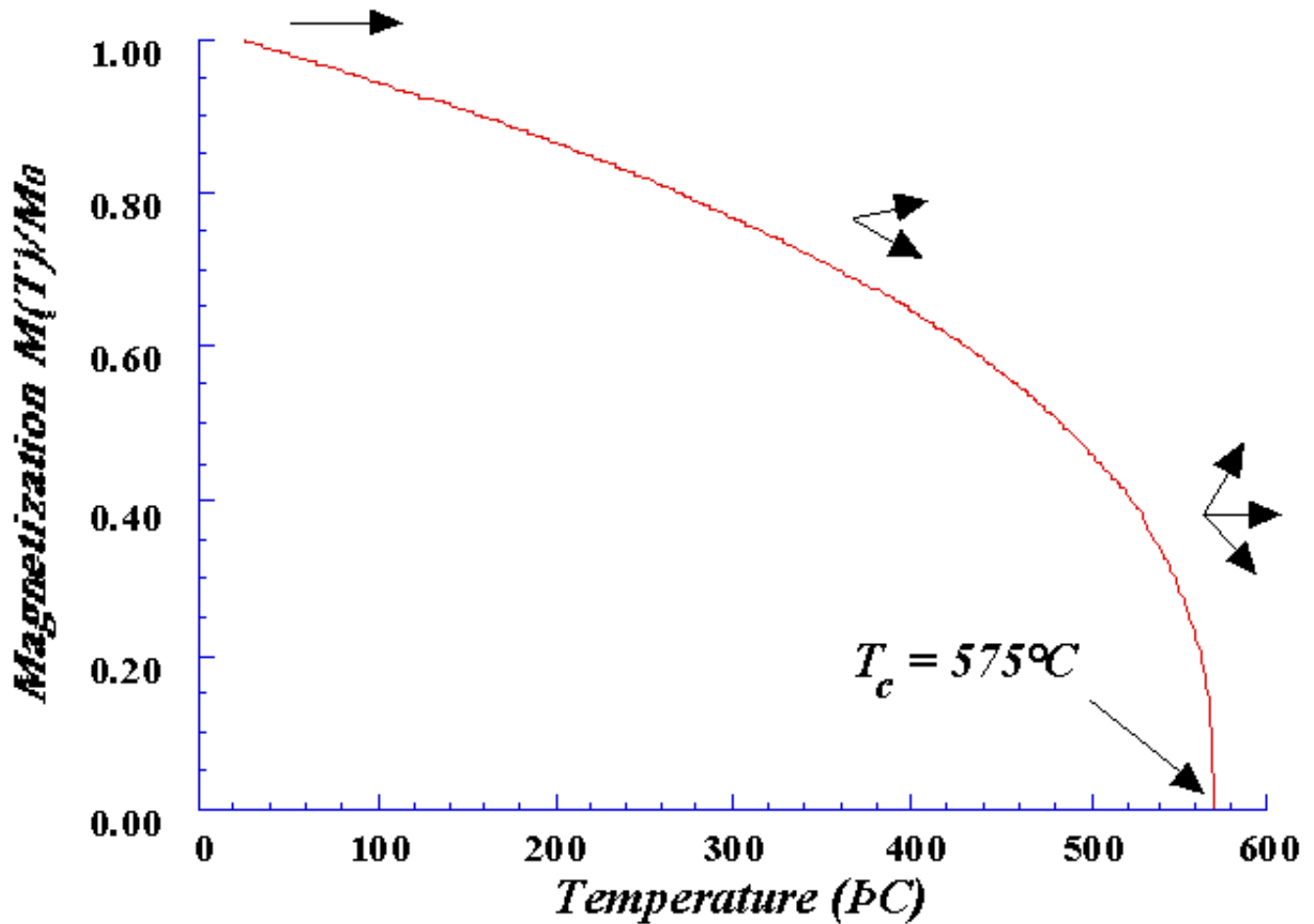
There is a big difference between paramagnetic and ferromagnetic susceptibility. As compared to paramagnetic materials, the magnetization in ferromagnetic materials is saturated in moderate magnetic fields and at high (room-temperature) temperatures:

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

Curie Temperature

Even though electronic exchange forces in ferromagnets are very large, thermal energy eventually

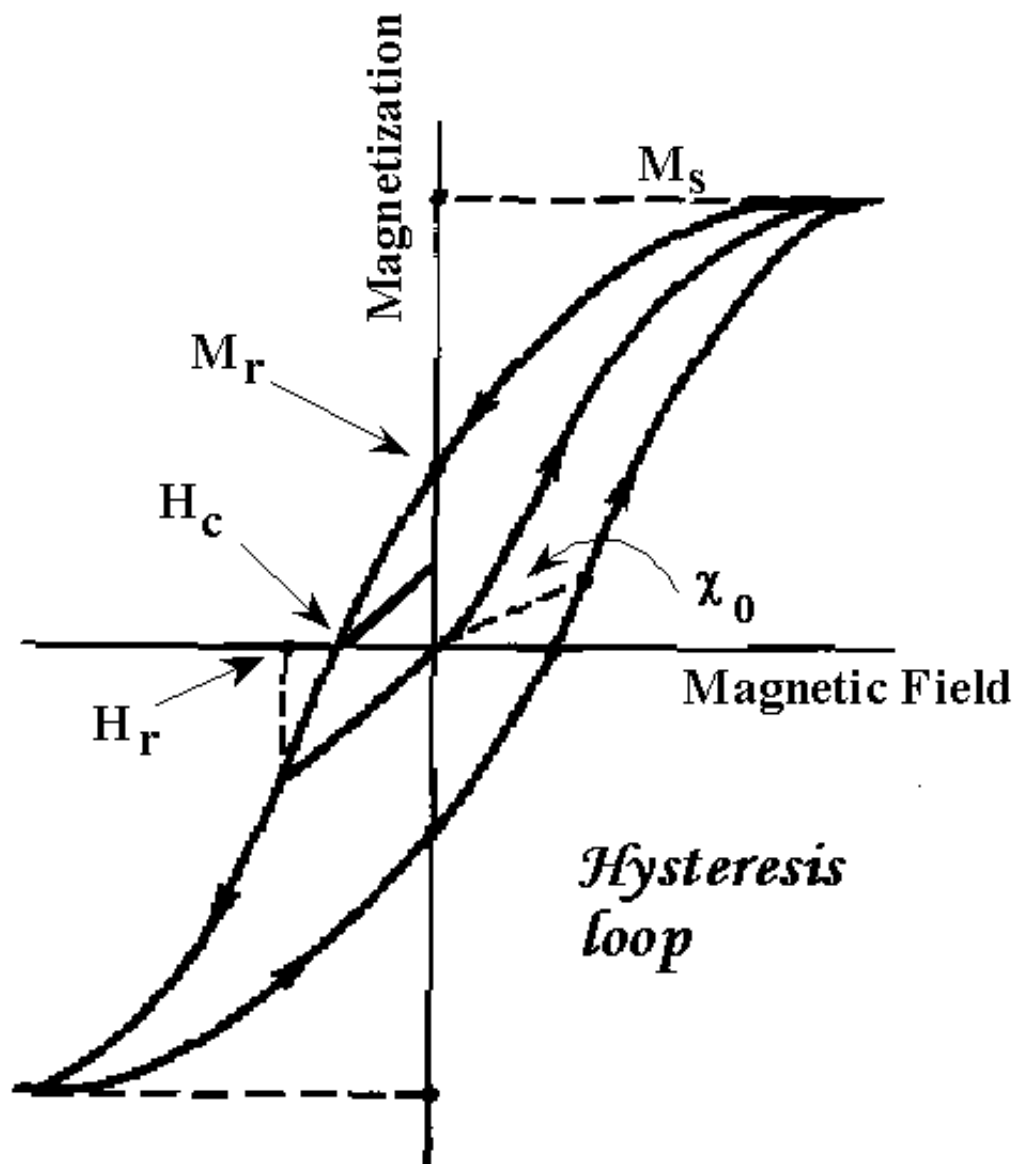
overcomes the exchange and produces a randomizing effect. This occurs at a particular temperature called the Curie temperature (T_c). Below the Curie temperature, the ferromagnet is ordered and above it, disordered. The saturation magnetization goes to zero at the Curie temperature. A typical plot of magnetization vs temperature for magnetite is shown below.



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.



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

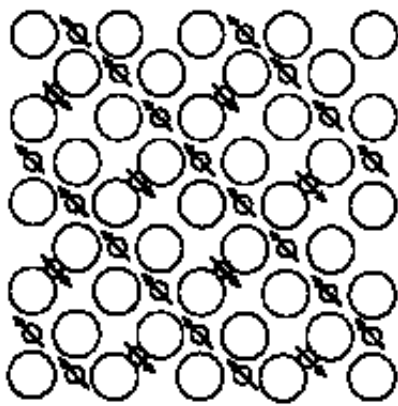
order of the earth's field (50-100 μT).

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.

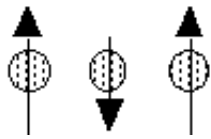
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4. Ferrimagnetism

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

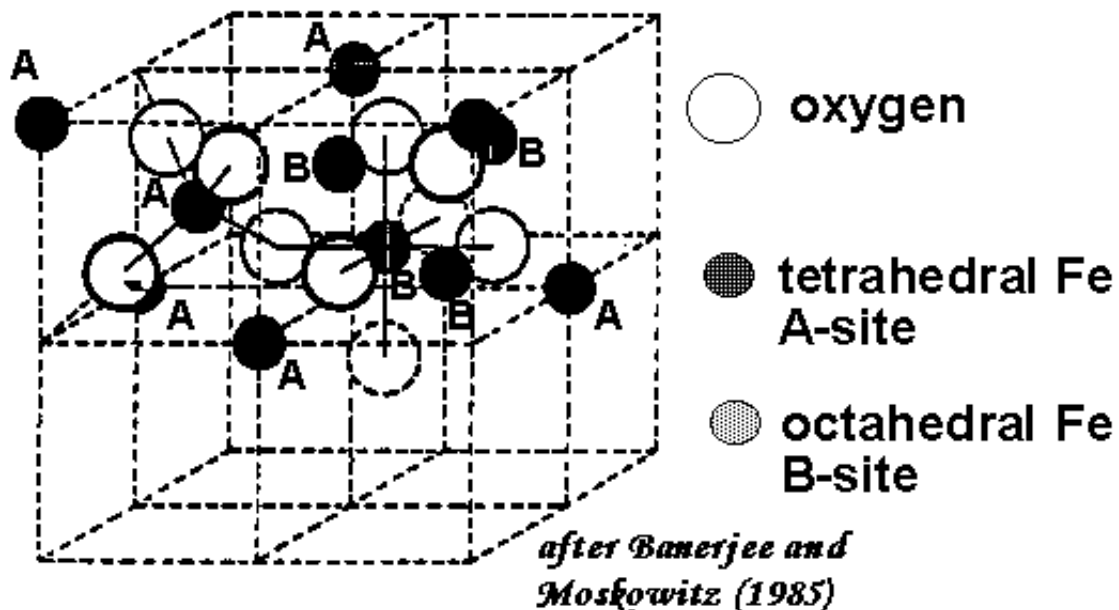


The magnetic structure is composed of two magnetic sublattices (called A and B) separated by oxygens. The exchange interactions are mediated by the oxygen anions. When this happens, the interactions are called indirect or superexchange interactions. The strongest superexchange interactions result in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



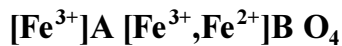
Magnetite, Fe_3O_4 crystallizes with the spinel structure. The large oxygen ions are close packed in a cubic arrangement and the smaller Fe ions fill in the gaps. The gaps come in two flavors:

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.

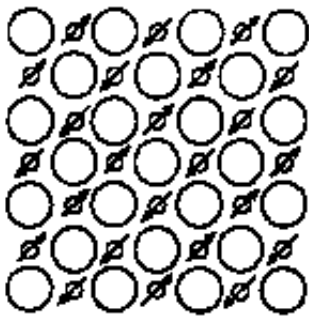
The structural formula for magnetite is



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+} .

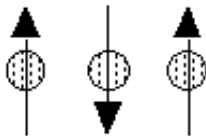
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5. Antiferromagnetism

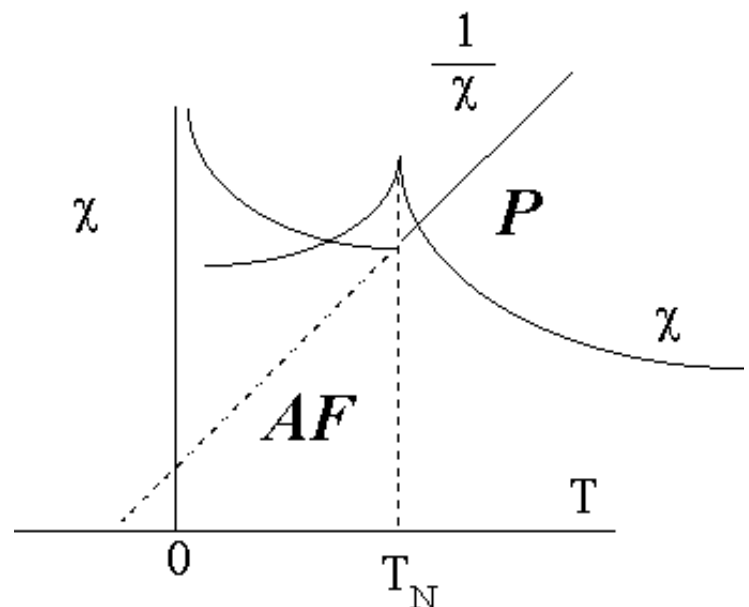


If the A and B sublattice moments are exactly equal but opposite, the net moment is zero. This type of magnetic ordering is called antiferromagnetism.

Antiferromagnetism

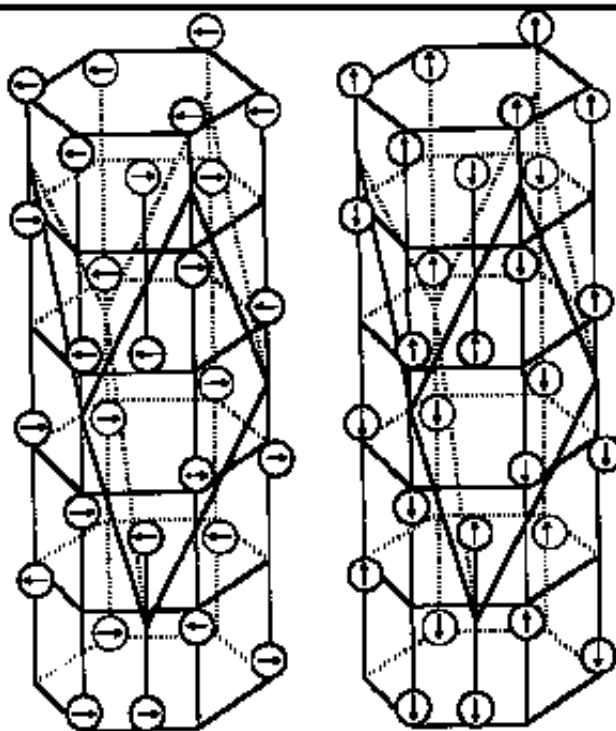


The clue to antiferromagnetism is the behavior of susceptibility above a critical temperature, called the Néel temperature (T_N). Above T_N , the susceptibility obeys the Curie-Weiss law for paramagnets but with a negative intercept indicating negative exchange interactions.



Crystal Structure of Hematite

Crystal Structure of Hematite



$T > -10^\circ C$

$T < -10^\circ C$

○ Fe^{3+} ion

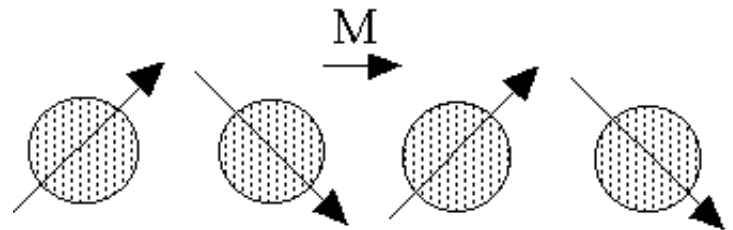
Hematite crystallizes in the corundum structure with oxygen ions in an hexagonal close packed framework. The magnetic moments of the Fe^{3+} ions are ferromagnetically coupled within specific c-planes, but

after Fuller (1987)

antiferromagnetically coupled between the planes.

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 ($\sigma_s = 0.4 \text{ Am}^2/\text{kg}$).

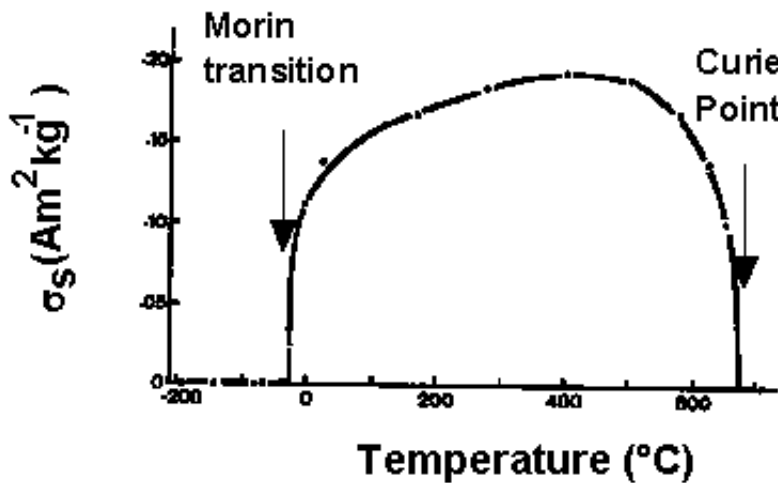
Below -10°C , the direction of the antiferromagnetism changes and becomes parallel to the c-axis; there is no spin canting and hematite becomes a perfect antiferromagnet.



Canted Antiferromagnetism

This spin-flop transition is called the Morin transition.

Hematite



after Dunlop (1971)

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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 Sulfides	MgFe ₂ O ₄	ferrimagnetic	440	21
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	
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

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