CHAPTER 2

LITERATURE REVIEW

2.1 History of magnetization

2.1.1 The definition of magnetic Terms

Magnetic materials have certain macroscopic properties that define what they are. These properties depend on some internal features of the material. To discuss them, we need to know the following definition.

2.1.1.1 Magnetic Field, H

At the macroscopic level, magnetic fields are produced when an electrical current flow in a conductor. The magnetic field produced by a permanent magnet is the result of the orbital motion and spin of the electrons. The unit of magnetic field strength is often defined in terms of the generation current, i.e., amp/turn/m.

2.1.1.2 Magnetic Induction, B

When a magnetic field is applied to a media, the density of lines of force within the media is known as the magnetic induction or magnetic flux density. The flux density in weber/metre^2 or tesla is also known as the magnetic induction (B) which is related to H by the permeability (μ) of the media. In many media, B is a linear function of H. In particular in a vacuum, we have

$$B = \mu_0 H \qquad (2.1)$$

where μ_0 is permeability of free space and is equal to $4\pi \times 10^{-7}$ henry per metre. In other media, particular ferromagnets and ferrimagnets, B often are not linear function of H. They are still related by permeability of medium through the equation

$$B = \mu H \qquad (2.2)$$

where μ is not necessary a constant. In ferromagnet, μ varies rapidly with H (Jiles,1998)

2.1.1.3 Magnetic Moment, m

Magnetic moment is an important and fundamental quantity in magnetism. The magnetic moment of current loop is the product of the current and the area enclosed by the loop, i.e,

$$m = iA \qquad (2.3)$$

where m is a magnetic moment. In the case of bar magnets, the magnetic moment is equal to the product of the pole strength in amp meter and the separation between the pole l in meters

$$m = pl \qquad (2.4)$$

The magnetic moment can also be expressed as the maximum torque on a magnetic dipole τ_{max} divided by B

$$m = \tau_{max}/B \qquad (2.5)$$

where the magnetic moment is measured in amp-metre^2 which is equal to current loop or to a bar magnet (William, 1996)

2.1.1.4 Magnetization, M

The moment per unit volume in the sample is intensity of magnetization or magnetization M

$$M = m/v \qquad (2.6)$$

The magnetization can also be referred to in terms of unit per mass. The specific magnetization σ is defined as

$$\sigma = M/\rho \qquad (2.7)$$

where ρ is the density. In the bar magnet with a flux density ϕ at the center of the bar and the dipole length is l, the magnetic moment m is given by m = $\phi l / \mu_0$. Since the magnetization M is defined as M = m/A l, we have

$$M = \phi / \mu_0 A = B / \mu_0 \qquad (2.8)$$

When a magnetic material placed in a magnetic field, both the magnetization M and magnetic field contribute to magnetic induction. B will be the vector sum of these two terms and we have

$$B = \mu_0 (H + M) \qquad (2.9)$$

2.1.1.5 Permeability and Susceptibility, μ, κ

The permeability μ is defined as

$$\mu = B / H \qquad (2.10)$$

and the susceptibility(κ) is defined as the ratio of the magnetization and the field, i.e.,

$$\chi = M / H \qquad . \qquad (2.11)$$

Thus

$$\mu = \mu_0 (1 + \chi) \qquad (2.12)$$

The ratio μ / μ_0 is equal to $1 + \chi$. μ_r is known as the relative permeability. The susceptibility is the main parameter that characterizes a magnetic material since it is the response of material to an applied field.

2.1.1.6 Hysteresis

The relation of magnetic flux and magnetic field is often referred to as hysteresis. It is used to obtain a great deal information about the material (Figure2.1).

2.1.1.6.1 Saturation Magnetization (M_s)

At the point of saturation magnetization (M_s), the maximum alignment of the atomic moment occurs and any additional increase in the magnetic field will produce very little increase in magnetic induction. The saturation magnetization depended only on the magnitude of the atomic magnetic moment m and the number of atom per unit volume n, Hence

$$M_s = nm \qquad (2.13)$$

M_s therefore depends only on the material present in a specimen and is not sensitive to the structure (Jiles, 1998).

2.1.1.6.2 Remanant Magnetization (M_r)

It is a measure of material's ability to retain a certain amount of residual magnetic field when the magnetizing force is removed after achieving saturation magnetization.

2.1.1.6.3 Coercivity, H_c

The magnetic field strength required to reduce the magnetic magnetization to zero is known as the coercivity; its unit is Oe or Am/m^{-1}. It is strongly dependent on the history of sample, being affected by such factor as heat treatment or deformation.

2.1.1.6.4 Energy Product, BH

The energy product comprises of magnetic field strength and coercivity. It describes the ability of permanent magnet to withstand the influence of a counteracting magnetic field. Additionally, the energy product is a measure of the useful flux that can be produced by the magnet in a given volume; its unit is KJm^{-3}. It is the maximum value of BH obtained in the second quadrant of hysteresis loop (Figure2.2).

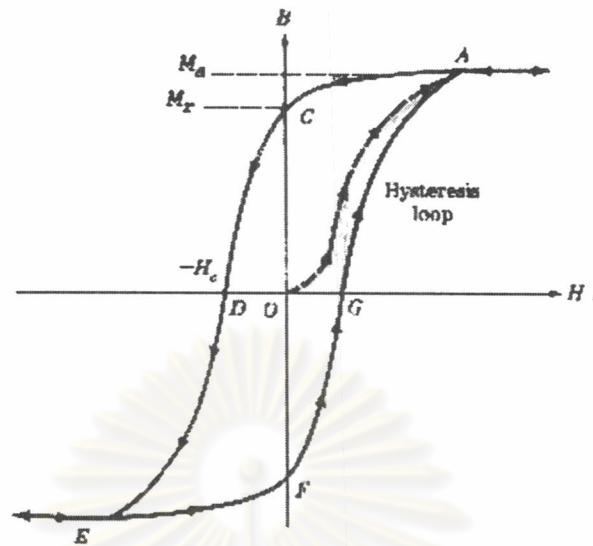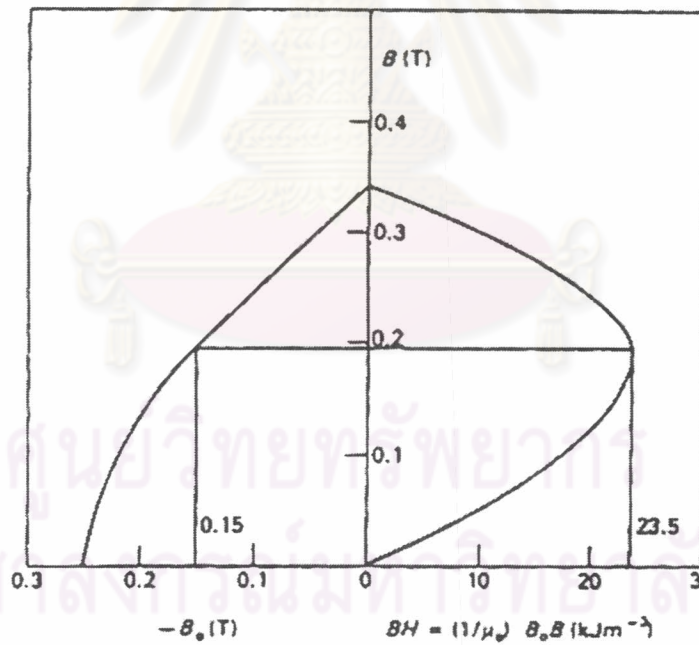Figure 2.1 The typical hysteresis of ferromagnetic material (William, 1996).

Figure 2.2 The energy product current of the barium ferrite (Jiles,1998).

2.1.2 Type of magnetism

The magnetic behavior of any material can be explained in term of the alignment of magnetic moment within those materials. Magnetic materials can be classified into 5 categories depending on the magnetic susceptibility of the material. The five categories are (1) diamagnetism, (2) paramagnetism, (3) ferromagnetism, (4) antiferromagnetism and (5) ferrimagnetism. The four first can be found in pure elements at room temperature, while the last group is only found in some ceramic oxide.

2.1.2.1 Diamagnetism

In a diamagnetic material, the induced dipole moment caused by an external field is opposite to the direction of the field. Diamagnetism leads to a very weak magnetization, which is, opposed to the applied field. Thus, χ is negative and is of the order of magnitude 10^{-5} or 10^{-6}. χ is independent of temperature. Examples of diamagnets are Ag, Au, Cu and Be.

2.1.2.2 Paramagnetism

Paramagnetism occurs when the induced magnetic moments are in the direction of the applied field. Paramagnetis have magnetic susceptibility in the range from 10^{-6} to 10^{-2}. There are a number of possible models for the paramagnetic behavior in materials, i.e., the Langevin model, the Curie model or the Pauli model (Cullity, 1972). The Langevin model describes paramagnetism in terms of the magnetic moment, which are localized at atomic or ionic sites in the material. This model states that each atom has a magnetic moment which is randomly oriented as a result of thermal agitation. The application of magnetic field causes the alignments of these moments. This leads to a low magnetization in the same direction as the applied field. As the temperature increases, the thermal agitation increases. It then becomes harder to align the atomic magnetic moments. The susceptibility therefore decreases. The relation between the susceptibility (χ) and temperature (T) is known as Curie law. It has the form:

$$\chi = C/T \qquad (2.14)$$

where C is the Curie constant.

The other model is Curie – Weiss model. It differs from the Langevin model in that it takes into account the interaction between neighboring spins. By including the interaction, Weiss found that

$$\chi = C/(T-\theta) \qquad (2.15)$$

Where θ depends on the nature of the interaction. In this equation θ can either be positive , negative or zero. For $\theta = 0$, the Curie-Weiss law reduces to the Curies law. If θ is positive, the material is ferromagnetic below the transition temperature and the value of θ corresponds to the transition temperature (Curie temperature, T_c). When θ is negative and the material will be an antiferromagnet below the transition temperature θ(now called the Neel temperature,T_N) . It is important to note that this equation is only valid when material is in a paramagnetic state. The Curie–Weiss law can applied to some metals such as rare-earth compounds.

The Pauli model of paramagnitism is true for material where the electrons are free to move. They can interact to form the conduction band. This is valid for most paramagnetic metals. In this model, the conduction electrons are essentially free to move and are said to be non localized. Under an applied field, an imbalance between numbers of electron of opposite spin is created. Since the net magnetization is equal to the difference in the number of magnetic moments pointing up and the number of magnetic moments pointing down, we get a low magnetization in the direction of the applied field.

2.1.2.3 Ferromagnetism

The ferromagnetism is produced when the spins of inner unpaired electrons are aligned with the crystal. In these material, the magnetic moment within atom are aligned parallel below the Curie temperature through the some quantum mechanical interactions between the ions with the unpaired electrons. Once the interaction is taken into account, the steps leading to the Curie – Weiss law can be used to obtained the temperature behavior of these materials. Ferromagnetic materials do not need an external field to have a net magnetization. The susceptibilities of ferromagnetic

materials are functions of both the applied field and the microstructures of the material. These material are compared in term of their saturation magnetization rather than their susceptibility. Examples of ferromagnetic materials are Fe, Co and Ni.

2.1.2.4 Antiferromagnetism

In antiferromagnetism, the exchange interaction between neighbouring ions led to an anti-parallel alignment of magnetic moment in the absence of an applied field. Therefore, the magnetic field produced by these magnetic moments cancel out. The materials appear to behave the same way as paramagnetic material. The susceptibility of antiferromagnet is slightly positive and is of the order of magnitude 10^{-6}. Examples of antiferromagnetic materials are Cr and Mn.

2.1.2.5 Ferrimagnetism

The exchange interaction lead to parallel alignment of atom in some crystal site and anti-parallel alignment occurs. Ferrimagnetism results if the alignment does not lead to the magnetization in one direction equal to the magnetization in the opposite direction. The net magnetization will therefore not be zero. As a group, ferrimagnet are call ferrites. These have low conductivity and this property makes them useful for many electronics application. Examples of ferrimagnet are Fe_2O_3 and $BaFe_{12}O_{19}$. The direction of magnetic moments for four of the categories are shown in figure 2.3

| Ferromagnetism | Antiferromagnetism | Ferrimagnetism | Paramagnetism |

Figure 2.3 Different forms of magnetic behavior

2.1.3   Unit system in magnetism

Unlike the units in mechanics, the units in magnetism are not simply related. The conversion from cgs to mks is simply based on the division by 10's. In magnetism, the conversion is much more complicated since two fields of science has contributed to its development. In physics the units for the currents are based on the concept of the force between two wires place one meter apart with the currents going in opposite directions in the two wires. In chemistry, the unit for the current is based on the number of electrons needed to deposit one mole of an element on one electrode during an electrolysis experiment. Three-unit system is currently in use: two systems for MKS (metre-kilograms-second), the Sommerfeld convention and the Kennelly convention, which has been renamed as the SI system. The third system is the CGS (centimetres-grams-second) system, which is also known as the gaussian. The CGS and SI system take different approaches. The former took an approach based on magnetostatics and the concept of the " magnetic pole", while the latter took an electrodynamic approach to magnetism based on electric current. The conversions between CGS and SI magnetic unit are as follow

$$1 \text{ oersteds} = (1000/4\pi) \text{ A m}^{-1} = 79.58 \text{ A m}^{-1}$$
$$1 \text{ gauss} = 10^{-4} \text{ T}$$
$$1 \text{ emu cm}^{3} = 1000 \text{ Am}^{-1}$$

Table 2 .1 Principle unit system uses in magnetism (Jiles,1998).

Quantity		SI (Sommerfeld)	SI (Kennelly)	EMU (Gaussian)
Field	H	A m^{-1}	A m^{-1}	oersteds
Induction	B	tesla	tesla	gauss
Magnetization	M	A m^{-1}	-	emu cc^{-1}
Intensity of Magnetization	I	-	tesla	-
Flux	ϕ	weber	weber	maxwell
Moment	m	A m^2	weber meter	emu
Pole strength	p	A m	weber	emu cm^{-1}
Field equation		$B = \mu_0(H+M)$	$B = \mu_0(H+I)$	$B = H+4\pi M$
Energy of moment (in free space)		$E = -\mu_0 m.H$	$E = -m.H$	$E = -m.H$
Torque on moment (in free space)		$\tau = \mu_0 m \times H$	$\tau = m \times H$	$\tau = m \times H$

2.1.4 Usage of magnetic materials.

Magnetic materials are used in a wide of application; from heavy current engineering such as electrical motor and generator to small-scale uses for example data storage information such as floppy dish. The two types of application require quite different magnetic properties. We will consider some applications and the properties they require.

2.1.4.1 Soft Magnetic Materials

Soft magnetic materials are those materials that are easily magnetized and demagnetized. They typically have intrinsic coercivity less than 1000 Am^{-1}. They find extensive application as a result of their ability to enhance the flux produced by an electrical current. The uses of soft magnetic materials fall into two general categories, a.c. and d.c. For a.c. applications, the soft magnetic materials are used mainly in transformer, motor core, and generator. The requirements for these applications are

materials, which have high peameability and saturation, low coercivity and low power loss as well as low conductivity. The most common materials used for these application are the silicon-iron alloys.

For d.c. application, the crucial use of soft magnetic materials are electromagnet and relays. These application generally required low coercivity and high permeability. For electromagnets, soft iron is still the most widely used material because it is relatively cheap and can produced high magnetic flux densities.

2.1.4.2 Hard Magnetic Materials

Hard magnetic materials, often refer to as permanent magnets, are magnets that retain their magnetism after being magnetized. Practically, hard magnetic materials are hardly to magnetized and have coercivity above 10 KAm^{-1} (125 Oe). Permanent magnet must be able to generate stable magnetic field without continuous expenditure of electric energy. The major application of permanent magnet are in electric motor, generators, loud speakers, moving coil meters, magnetic separators, control device for electron beams such as in TV sets, frictionless bearings and magnetic levitation system and so on. The desirable properties of permanent magnet are therefore high coercivity and high remanence as well as large magnetization. Additionally, the squareness ratio (Mr/Ms) must also be closed to 1 in order to ensure a large remanence. A number of different materials have been used as permanent magnets i.e. magnetite, steel, alnico alloys, hard ferrite, platinum-cobalt, samarium-cobalt, neodymium-iron-boron, samarium iron-nitride.

2.1.4.3 Magnetic Recording

The first magnetic sound recording was carried out in 1898 by the Danish inventor, Valdemar Poulsen. The familiar oxide tapes used for audio recording were developed by 3M in 1974. Nowadays, magnetic recording of sound image and digital data on magnetic media are omnipresent in our daily life. Magnetic materials find application in storage media because they can be made to point in one direction or the other if one place them in an external magnetic fields. This allows data be recorded or read. Magnetic recording can either be analog, as in audio recording of signals on

magnetic tape, or digital, as used in the storage of information data on magnetic disk for computer application.

Magnetic recording materials have some characteristics in common with permanent magnets. They need to have a relatively high saturation magnetization and remanant to give as large signal as possible during the reading process. The coercivity has to be sufficient enough to prevent erasure, but small enough to allow the material to be reused for recording. Their coercivity should be in the range of 20-100 KAm^{-1} which are common in magnetic recording and disk. The most widely used magnetic materials are gamma ferric oxide, cobalt surface- modified gamma ferric oxide, chromium oxide, hexagonal ferrite and so on.

2.2   Survey of ferrite materials

Ferrites, which belong to ferrimagnetism group, play important roles in many industries and are used in many electronic devices. Ferrites were developed into commercially useful materials during 1933-1945 (Cullity,1972). There are 3 groups of ferrites that are divided according to their crystal structure, named cubic ferrite, hexagonal ferrite and garnet. We only concerned here with the cubic and hexagonal ferrite.

2.2.1 Cubic ferrite (spinel ferrite)

Spinel ferrites have the general chemical formula MFe_2O_3, where M is a divalent metal ion, usually with an ionic radius in the rage 0.06-0.1 nm. They are usually Mn, Ni, Fe, Co, Mg, etc. The crystal structure of spinel ferrite consists of a face center cubic closed – packed structure comprising of oxygen ion containing 32 octahedral sites and 64 tetrahedral sites. Only 8 of the tetrahedral (A site) and 16 of the octahedral site (B site) are occupied by the metal ions, as illustrate in Figure. 2.4
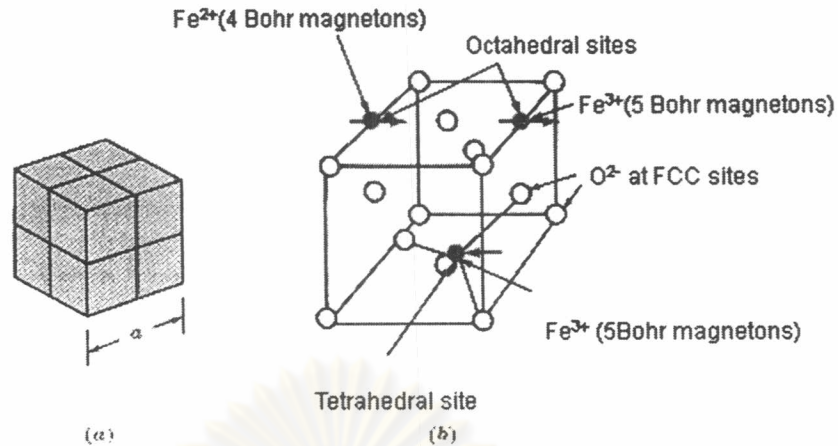
Figure 2.4 Crystal structure of cubic ferrite,: a) a unit cell of MFe_2O_4 b) The subcell of Fe_3O_4 (William, 1996)

The spinel ferrites have two idealized magneticstructures. First, there is the normal spinel in which all divalent ions are on the tetrahedral site, e.g. $ZnFe_2O_4$ and $CdFe_2O_4$. The other is the inverse spinel in which the 8 tetrahedral site are filled with the trivalent ions and 16 octahedral site are equally occupied by the remaining divalent and the trivalent ion. Examples of the latter are Fe_3O_4, $NiFe_2O_4$ and $CoFe_2O_4$. In some ferrites two kinds of divalent ion can be found, e.g. $(Ni,Zn)Fe_2O_4$. All of the magnetic properties of these ferrites depend on the interaction between the ions on the tetrahedral (A) and octahedral (B) sites. The distribution of the ions on these site is therefore of critical importance. The factor which determine distribution of the cation on A and B sites are the radius, the electronic configuration, the electrostatic energies and the polarization effect. Some properties of ferrite e.g., the lattice parameter, the ion moment, the Curie temperature and the density are showed in table 2.2. Generally, single type spinel–ferrite are seldom used in actual application. In most cases, mixed ferrite which are prepared from two different kind of single type of spinel ferrites are used. These exhibit more favorable magnetic properties, which can be applied in a wide range of applications.

Table 2.2 The properties of cubic ferrite at room temperature (Cullity, 1972 and McCurries, 1994)

Formula	Structure	Lattice patameter (nm)	Ion moment (μB)	Curies temperature T_c (°C)	Density (103 Kgm^{-3})
$MnFe_2O_3$	mostly normal	0.850	5.0	300	5.00
$FeFe_2O_4$	inverse	0.839	4.1	585	5.24
$CoFe_2O_4$	inverse	0.838	3.7	520	5.29
$NiFe_2O_4$	inverse	0.834	2.3	585	5.38
$CuFe_2O_3$	inverse	0.845	1.3	455	5.42
$MgFe_2O_4$	mostly inverse	0.836	1.1	440	4.52
$Li_{0.5}Fe_{2.5}O_4$	-	0.833	2.6	670	4.75
γ-Fe_2O_3	inverse	0.834	2.3	575	4.89
$ZnFe_2O_3$	normal	0.840	0.0	-	5.40
$CdFe_2O_3$	normal	0.873	0.0	-	5.76

The spinel ferrites are useful due to their high-permeability and low hysteresis loss as well as high coercivity. Application of spinel ferrite can be classified into three main groupings according to the frequency of the magnetic field of the device in which it use

1) Low-frequency, high-permeability application , e.g., Mn-Zn ferrite.

2) High frequency low-loss application application, e.g., Ni-Zn ferrite.

3) Microwave application

There are many factors which can change their magnetic properties, e.g., the composition, the grain size, impurities, the size and distribution of the porosity. Using different processing methods, e.g., preparation technique, heat treatment and others, can control these factors. Presently, there are many techniques using for the preparing the cubic ferrite, e.g., conventional ceramic method, co-precipitation, sol gel. Among these techniques, the conventional ceramic method is mostly used for commercial ferrite.

2.2.2 Hexagonal Ferrite

Hexagonal ferrites are another group of ferrimagnets. These materials are of interest because of their high magnet crystalline anisotropy, high coercivity, etc. Their crystal structure consists of S and R layers which we can view as the chemical radicals $(Fe_6^{3+}O_8)^{2-}$ and $(Fe_6^{3+}O_8)^{2-}$, respectively. There are 6 classes of hexagonal ferrites which having following stacking:

1)	M	type	$BaFe_{12}O_{19}$	RS	Stacking
2)	U	type	$Ba_4 **Me_2 Fe_{36} O_{60}$	M_2*Y	Stacking
3)	Z	type	$Ba_6 Me_4 Fe_{48} O_{82}$	M_2Y_2	Stacking
4)	Y	type	$Ba_2 Me_2 Fe_2 O_{22}$	TS	Stacking
5)	X	type	$Ba_2 Me_2 Fe_{26} O_{46}$	M_2S	Stacking
6)	W	type	$Ba Me_2 Fe_{16} O_{27}$	MS	Stacking

$$*Y \quad = \quad ST\ Stacking$$

$$**Me \quad = \quad divalent\ ion$$

Among these hexagonal ferrites, the M type $(BaFe_{12}O_{19})$ is the best known and most widely used in commercial applications. Discussion will focus only on the M type ferrite.

2.2.2.1 Barium Ferrite (BaF)

2.2.2.1.1 Crystal and Magnetic Structure

Barium M-hexaferrite (BaF) has a complex crystal structure. There are 64 ions per unit cell In the unit cell, there are 24 Fe^{3+} atoms distributed over the five distinct systems within the R and S blocks. In the S block, there are 2 spin-up sites having octahedral symmetry and 4 spin-down sites having tetrahedral symmetry. In the R block, there is 1 spin-up site having trigonal or bipyramid symmetry, 2 spin-down sites having octahedral symmetry. There are 3 spin-up sites having octahedral symmetry, which is located between S and R block (Table 2.3 and Figure 2.5). These sites are occupied by the trivalent Fe^{3+} ions.

Table 2.3 Structure and magnetic characteristic of the magnetic sublattices in the BaFe$_{12}$O$_{19}$(Wohfarth, 1982)

Ion	Coordination	Block	Number of ions per unit formula*	Spin direction
Fe1	octahedral	S	1	up
Fe2	Five-fold	R	1	up
Fe3	tetrahedral	S	2	down
Fe4	octahedral	R	2	down
Fe5	octahedral	R-S	6	up

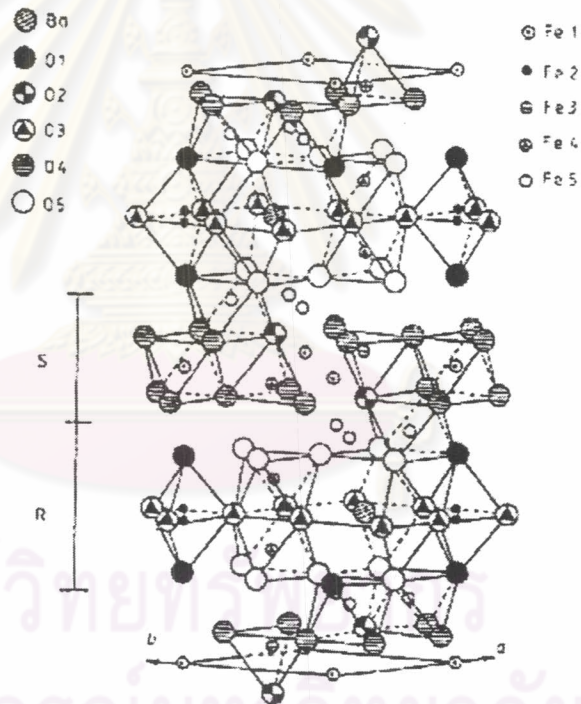1 unit cell of Ba Fe$_{12}$ O$_{19}$ consists 2 unit formula

Figure 2.5 Crystallographic structure and cationic polyhedra of the BaFe$_{12}$O$_{19}$(Obradors et al., 1986)

2.2.2.1.2 Magnetic Properties

(1) Magnetization

The magnetization arises from the moments of the Fe ions located on the different layers. The interactions between the Fe^{3+} ions located in neighboring layers are

antiferromagnetic and so the alignments of the spins on the adjacent layers are antiparallel. Therefore the total magnetization at temperature (T) can be expressed as

$$M_s(T) = 6\,\sigma_k(T) - 2\sigma_{f1}(T) - 2\sigma_{f2} + \sigma_b(T) + \sigma_a(T) \qquad (2.16)$$

Where σ_k, σ_{f1}, σ_{f2}, σ_b and σ_a denote the magnetization of Fe^{3+} in each sublattice. Since the magnetic moment of Fe^{3+} is 5 μ_B at 0 K, the total total magnetization will be 20μ_B. Betant et al. and Shrink et al. obtained M_s in the range of 70. –72 emu/g and Belov et al. pointed out that the spontaneous magnetization of BaF along the c-axis is somewhat greater than that in the perpendicular direction (Wohlfarth, 1982). Later,the saturation magnetization per gram σ_s of BaF has been given by many author (Zhou et al., 1994, Han et al., 1994, Zhong et al., 1997). The values range between 63-70 emu/g and are close to the values taken to be typical of BaF ferrite 70 emu/g.In Figure 26 ,Taube et al.found that the saturation magnetization versus temperature curves appears to be a straight line (line no.1) and Casimir et al. found this relation was concave (line no 2) . Both of them reported that a steep slope found in the temperature range of 200 and 600 K. (Wohlfarth).
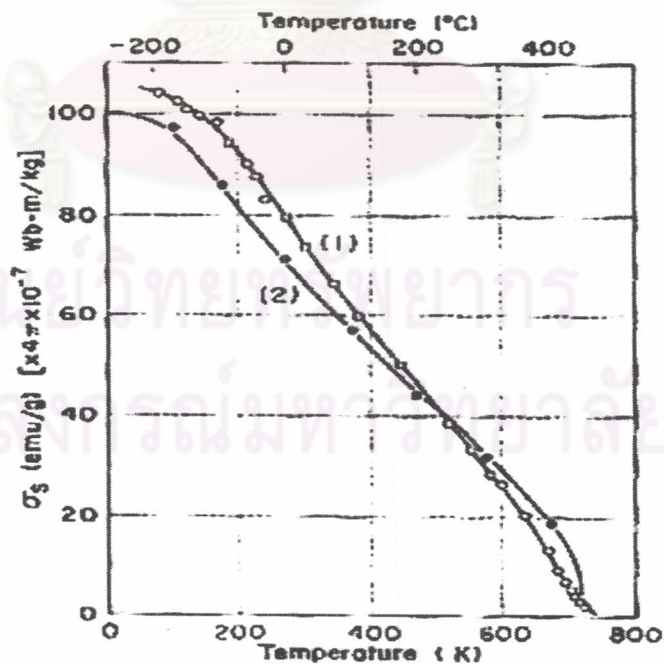

Figure 2.6 The specific saturation magnetization versus temperature for BaFe$_{12}$O$_{19}$ (Wohlfarth, 1982)

(2) Magnetocrystalline Anisotropy

One of the most important properties of BaF is its very high uniaxial magnetocrystalline anisotropy. For single crystal of BaF, the easy direction of magnetization is in the direction of <0001>. When the direction of the magnetization in BaF is expressed in polar coordinate, the uniaxial magnetization anisotropy is given by the relation

$$E = K_0 + K_1 \sin_2 \theta \qquad (2.17)$$

Where θ is the angle between the magnetization vector and the c axis and K_1 is the magnetocrystalline constant. In terms of the anisotropy field H_A, we have

$$H_A = 2 K_1 / \mu_0 M_s \qquad (2.18)$$

It is easy to estimate the value of H_A from the data of K_1 and M_S. The magnetocryatlline constant (k_1) and the anisotropy field of barium ferrrite are temperature – dependent as seen in Figure 2.7and Figure 2.8.
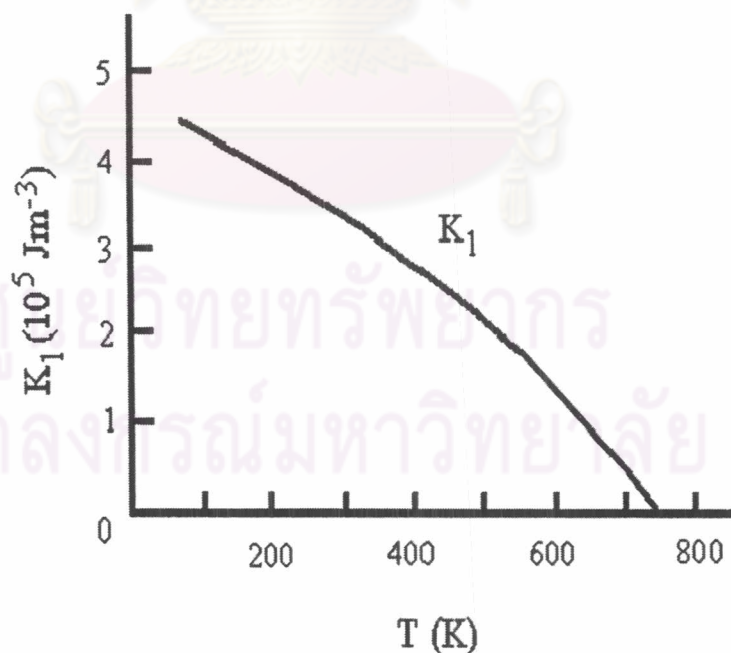

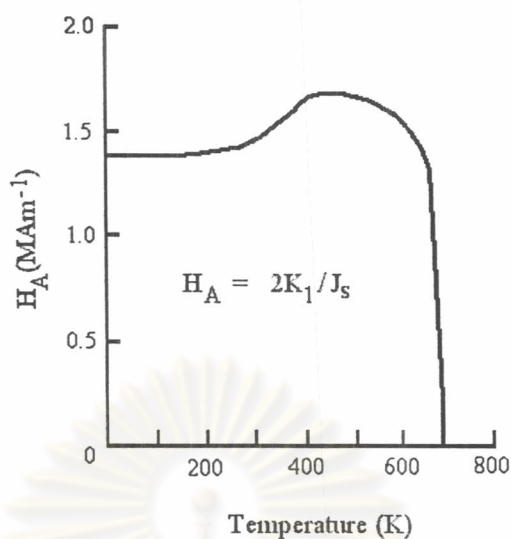Figure 2.7 Effect of temperature on the uniaxial magnetrocrystalline anisotropy coefficient (K_1)for $BaFe_{12}O_{19}$ (Thongmee, 1999)

Figure 2.8 Effect of temperature on the anisotropy field (H_A) of $BaFe_{12}O_{19}$ (Thongmee, 1999)

The high anisotropy of BaF is very important to its use as a permanent magnet. The anisotropy can be enhanced by the preparation of crystal–oriented or direction–oriented samples.

(3) Coercivity force

The coercivity (H_c) originates from the magnetocrystalline anisotropy. The magnetization is particularly uniaxial for the hexagonal close packing of $BaFe_{12}O_{19}$, $SrFe_{12}O_{19}$ and $PbFe_{12}O_{19}$. Stoner and Wohlfarth obtained the relation between H_c, K_1 and M_s for randomly oriented particle

$$H_c = \alpha \left[2K1/ M_s - BM_s \right] \tag{2.19}$$

Where α is a geometrical parameter and is 0.48 for the case of randomly oriented and B is the demagnetization constant.

The highest coercivity of BaF is observed when the material is ground to fine powder or is in form of sintered compact of powder. In addition, using different dopants and concentration can control the coercivity of BaF. The coercivity of BaF has been studied by Pal et al. (1997) who found that the substitution of Bi^{3+} into the BaF led

to an initial increase in H_c. Kuznetsov et al. (1999) reported similar behavior when Cr^{2+} was substituted into the BaF. Kuo et al. (1993) found that the H_c decreasing when increasing amounts of Co^{2+}-Sn^{4+} were substituted in. Fang et al. (1999) attributed the decrease in the H_c seen in Zn^{2+} Sn doped BaF to the decrease in the anisotropy field caused by the Zn^{2+} +Sn^{+4} substitution. BaF is one of the materials, which has high potential for use as a high-density perpendicular magnetic recording material. Presently, much attention has been paid to the replacement of the Fe ions in BaF, in order to control the anisotropy and the coercivity.

2.3 Vibrating sample magnetometer

Vibrating sample magnetometer (VSM) system are used to measure the magnetic properties of material as a function of magnetic field, temperature and time. It is the most common measurement method employed for hysteresis loop determination at ambient temperature. VSM is suitable for research and development, production testing, quality and process control. Powder, solids, liquids, single crystals and thin film can be measured by VSM. Figure 2.9 showed the picture of vibrating sample magnetometer.

Principle of operation

When material is placed within a uniform magnetic field, H, a magnetic moment m will be induced in the place sensing coils. This is made to undergo sinusoidal motion, i.e. mechanically vibrated. The resulting magnetic flux change will induced a voltage in the sensing coils that is proportional to the magnetic moment of the sample. During the measurement, the sample is vibrating at a standardized frequency ($\sin \omega t$). H does not depend on t but M depend on t as shown in the following equation,

$$V = -NA\, dB/dt$$

$$= -NA\mu_0 dB/dt\,(H+M)$$

$$= -NA\mu_0 dH/dt - NA\mu_0 dM/dt$$

$$= 0 - NA\mu_0 dM_0 \sin\omega t$$

$$= -NA\mu_0 \omega M_0 \cos\omega t$$

$$= \alpha M_0 \cos\omega t$$

where V is the Induction voltage, t is time, N is the number of coil, A is area of coil, M is magnetization, H is magnetic field and μ_0 is permeability. By this method, the signal is directly proportional to magnetization.
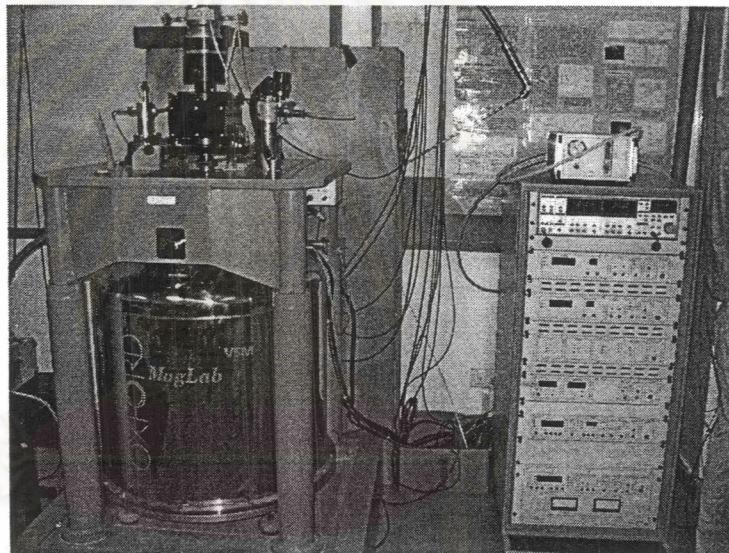

Figure 2.9 Vibrating sample magnetometer

2.4 Mossbauer spectroscopy

When a Fe or Sn nucleus is placed in a magnetic environment, the interaction between the nuclear spin I and the internal magnetic fields will cause a shift in the energy of the nuclear levels of the nucleus. The differences between the excited levels and ground states of the nucleus will be different from those of Fe or Sn nucleus sitting in a different environment. Because the absorption of radiation by the ground state will cause the nucleus to go into the excited level, the energy of the radiation must be exactly the difference in the energies of the two states of the nucleus. If the radiation is

the result of the transition of a second nucleus in a different magnetic environment, the absorption of the radiation by the first nucleus would not be possible. Transitions would only be possible if the energy of the incident radiation could be changed so that it would be in resonance with the difference in the energy levels of the first nucleus. This could be done by moved the second nucleus either towards or away from the first nucleus. The resulting Doppler shift would change the energy of the radiation.

Mossbauer spectroscopy essentially the recording of the radiation absorbed by the first nucleus as the second nucleus is being moved at different velocities. Several types of information may be obtained from Mossbauer spectra i.e.

Hyperfine magnetic field, (H_{hpf})

Interaction of the dipole moment of the nucleus and a hyperfine magnetic field cause a splitting of the nucleus energy level, resulting in six peaks for ^{57}Fe spectra .For the ideal random absorber with no quadrupole interaction the linewidths of the peak are equal with intensity ratio 3:2:1:1:2:3. The separation of peaks 1 and 6 is proportional to the magnitude of the magnetic field causing the energy shift. The unit of hyperfine magnetic field is tesla.

Isomer shift (IS)

Energy differences between source and absorbed nuclei resulting from effects including differences in valence state, spin state and coordination of absorber atom. Experimentally one observes a single line shifted from a reference zero point by isomer shift. The unit of hyperfine magnetic field is mm s^{-1}.

Quadrupole splitting (Δ)

Splitting of the energy level cause by interaction between the nuclear quadrupolar moment and electric field gradient at the nucleus and depend on the valence and spin state of the absorber atoms, as well as the coordination and degree of distortion of the crystallographic site. Experimentally one observed a doublet in ^{57}Fe

specctra with component of equal intensity and linewidth in the ideal random absorber case. The unit of quadrupole splitting is mm s^{-1}.

Line width (Γ)

Full width at half maximum of the peak height. Peak can be broadened beyond the natural line width by effect due to equipment, the source and the sample. The unit of quadrupole splitting is mm s^{-1}.

Relative area

Relative proportion of subspectrum area to the total area. Each site normally contribute a subspectrum whose area is approximately related the abundance of that particular site within the absorber.

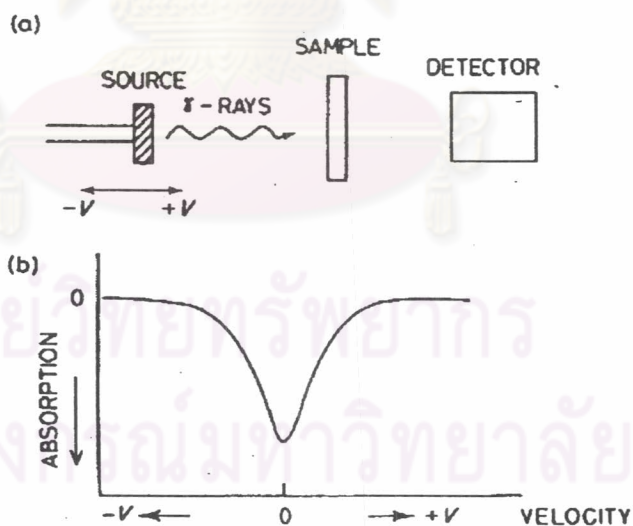A schematic illustration of Mossbauer spectroscopy was shown in Figure 2.10.

Figure 2.10 (a) The Mossbauer effect. The energy of the γ-rays is modified when emitted from a moving source (Doppler effect). (b) Typical single line spectrum obtained when source and sample are identical (West, 1999)