

Chapter One

Introduction

1.1 Prelude

All materials exhibit magnetism, but magnetic behavior depends on the electron configuration of the atoms and the temperature. The electron configuration can cause magnetic moments to cancel each other out (making the material less magnetic) or align (making it more magnetic). Increasing temperature increases random thermal motion, making it harder for electrons to align, and typically decreasing the strength of a magnet. Magnetism may be classified according to its cause and behavior. The main types of magnetism are (chiba et al., 2005):

Diamagnetism: All materials display diamagnetism, which is the tendency to be repelled by a magnetic field. However, other types of magnetism can be stronger than diamagnetism, so it is only observed in materials that contain no unpaired electrons. When electrons pairs are present, their "spin" magnetic moments cancel each other out. In a magnetic field, diamagnetic materials are weakly magnetized in the opposite direction of the applied field. Examples of diamagnetic materials include gold, quartz, water, copper, and air.

Paramagnetism: In a paramagnetic material, there are unpaired electrons. The unpaired electrons are free to align their magnetic moments. In a magnetic field, the magnetic moments align and are magnetized in the direction of the applied field, reinforcing it. Examples of paramagnetic materials include magnesium, molybdenum, lithium, and tantalum.

Ferromagnetism: Ferromagnetic materials can form permanent magnets and are attracted to magnets. Ferromagnets have unpaired electrons, plus

the magnetic moment of the electrons tends to remain aligned even when removed from a magnetic field. Examples of ferromagnetic materials include iron, cobalt, nickel, alloys of these metals, some rare earth alloys, and some manganese alloys.

Antiferromagnetism: In contrast to Ferromagnets, the intrinsic magnetic moments of valence electrons in an Antiferromagnetism point in opposite directions (anti-parallel). The result is no net magnetic moment or magnetic field. Antiferromagnetism is seen in transition metal compounds, such as hematite, iron manganese, and nickel oxide.

Ferrimagnetism: Like Ferromagnets, Ferrimagnets retain magnetization when removed from a magnetic field, but neighboring pairs of electron spins point in opposite directions. The lattice arrangement of the material makes the magnetic moment pointing in one direction stronger than that pointing in the other direction. Ferrimagnetism occurs in magnetite and other ferrites. Like Ferromagnets, Ferrimagnets are attracted to magnets. There are other types of magnetism, too, including super Paramagnetism, metamagnetism, and spin glass (Schweitzer et al., 2009; Jim Wilson, 1999).

1.2 Research Problem

Study on the classes magnetism with detailed and the application to the classes magnetism materials.

1.3 Literature Review

In 1976 the Tsuneharu Takeda et al. studied the surface magnetism of f.c.c. heisenberg ferromagnets. II. Magnetic field dependence. He found the magnetic field dependences of the surface magnetization are evaluated for f.c.c. Heisenberg Ferromagnets in the mean field approximation. Two different kinds of external magnetic fields, H and H_s , are assumed to exist;

the former is uniform over whole crystal and the latter is localized in the surface layer. The weak field limit is examined in detail. It is found that the susceptibility of the surface layer with respect to the uniform field, H , varies in proportion to $|T-T_c|^{-1/2}$ for both above and below the Curie temperature T_c and that that with respect to the local field, H_s , varies as const. $-(T-T_c)^{1/2}$ for $T>T_c$ and as const. $-(T_c-T)$ for $T<T_c$. These temperature dependences are also confirmed by the phenomenological treatments based on the Ginzburg-Landau equation. Validity of the Surface Sheet Model (SSM) is demonstrated.

In 1979 the Sheng-Wei Wang et al. studied the spin polarization effect in the theory of magnetic scattering from antiferromagnetic NiO (111) surfaces by polarized low energy electron diffraction. He found the dynamical calculations are performed to determine the differential cross section of low energy electrons scattered from antiferromagnetic NiO (111) surfaces. We find that the spin-dependence of this quantity with respect to the incident electron polarization depends strongly on: (1) the magnetization of the topmost layer, (2) the exchange potential model used, and (3) the incident beam angle.

In 1982 the Carl Rau studied the electron spin polarization esp at surfaces of ferromagnetic metals. He found the Fundamental information on surface magnetic order (SMO) of ferromagnetic metals can be obtained from electron-capture, photoemission, fieldemission, spin-dependent tunneling and spin-polarized LEED experiments. The different techniques, new experimental advances and developments are discussed with particular emphasis given to electron-capture spectroscopy. This review will focus on new experimental and theoretical results (long-range and "local" SMO of ferro- and antiferromagnetic metals, surface states, SMO of thin films, new magnetic surface phases, magnetic surface reconstruction, chemisorption) obtained in the years past which have brought outstanding

progress towards a deeper comprehension of the physics of ferromagnetism and towards the unravelling of the physical processes inherently involved in the various methods for spin spectroscopy. Recent data on the SMO received from experiments performed at surfaces of single crystals of 3d-TM and 4f-RE metals reveal new scientific insights and perspectives for the theoretical analysis of experimental results within the framework of the currently refined knowledge about ferromagnetism.

In 2018 the Pierce et al. studied the A polarized leed Of surface magnetism. He found the pierce et al studied polarized leed of the surface magnetization of ferromagnetic Ni(110) has been observed via the use of a spin polarized electron beam. The spin dependence of the scattered electron intensity was measured as a function of external magnetic field strength and temperature.

1.4 Objectives of the Study

The definition and explanation of the classes' magnetism; also a highlight on the classes' magnetism materials, precisely to determinate properties of each class and finally application of these materials.

1.5 Presentation Of The Thesis

In this research is consist of four chapters, chapter one views an introduction and literature review, chapter two consist classes of magnetism while chapter three consist contracture and application of classes magnetism materials, and finally chapter four for conclusion and recommendations.

Chapter Two

Classes of Magnetism

2.1 Introduction

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 (Croot, 1995) .

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

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 ferromagnetic 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".

2.2 Diamagnetism

Diamagnetic materials are repelled by a magnetic field; an applied magnetic field creates an induced magnetic field in them in the opposite

direction, causing a repulsive force. In contrast, paramagnetic and ferromagnetic materials are attracted by a magnetic field. Diamagnetism is a quantum mechanical effect that occurs in all materials; when it is the only contribution to the magnetism, the material is called diamagnetic. In paramagnetic and ferromagnetic substances the weak diamagnetic force is overcome by the attractive force of magnetic dipoles in the material. The magnetic permeability of diamagnetic materials is less than μ_0 , the permeability of vacuum. In most materials diamagnetism is a weak effect which can only be detected by sensitive laboratory instruments, but a superconductor acts as a strong diamagnetism because it repels a magnetic field entirely from its interior.

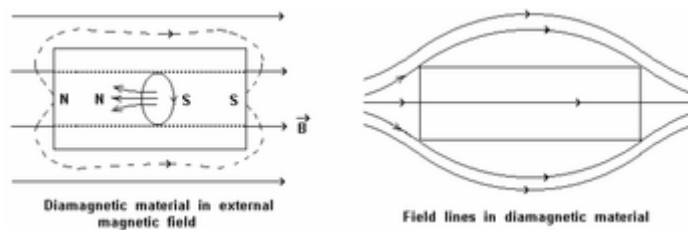


Figure (2.1): Diamagnetic material interaction in magnetic field.

Diamagnetism was first discovered when Sebald Justinus Brugmans observed in 1778 that bismuth and antimony were repelled by magnetic fields. In 1845, Michael Faraday demonstrated that it was a property of matter and concluded that every material responded (in either a diamagnetic or paramagnetic way) to an applied magnetic field figure (2.1). On a suggestion by William Whewell, Faraday first referred to the phenomenon as diamagnetic (the prefix dia- meaning through or across), then later changed it to diamagnetism (T.Lembke, 2005; Du Tremolet de Lacheisserie et al., 2005).

2.3 Paramagnetism

Paramagnetism is a form of magnetism whereby certain materials are weakly attracted by an externally applied magnetic field, and form internal, induced magnetic fields in the direction of the applied magnetic field. In contrast with this behavior, diamagnetic materials are repelled by magnetic fields and form induced magnetic fields in the direction opposite to that of the applied magnetic field. Paramagnetic materials include most chemical elements and some compounds; they have a relative magnetic permeability slightly greater than 1 (i.e., a small positive magnetic susceptibility) and hence are attracted to magnetic fields. The magnetic moment induced by the applied field is linear in the field strength and rather weak. It typically requires a sensitive analytical balance to detect the effect and modern measurements on paramagnetic materials are often conducted with a SQUID magnetometer (Platonis Opera et al., 1839).

Paramagnetism is due to the presence of unpaired electrons in the material, so all atoms with incompletely filled atomic orbitals are paramagnetic. Due to their spin, unpaired electrons have a magnetic dipole moment and act like tiny magnets. An external magnetic field causes the electrons' spins to align parallel to the field, causing a net attraction. Paramagnetic materials include aluminum, oxygen, titanium, and iron oxide (FeO).

Unlike ferromagnets, paramagnets do not retain any magnetization in the absence of an externally applied magnetic field because thermal motion randomizes the spin orientations. (Some paramagnetic materials retain spin disorder even at absolute zero, meaning they are paramagnetic in the ground state, i.e. in the absence of thermal motion.) Thus the total magnetization drops to zero when the applied field is removed. Even in the presence of the field there is only a small induced magnetization because

only a small fraction of the spins will be oriented by the field. This fraction is proportional to the field strength and this explains the linear dependency. The attraction experienced by ferromagnetic materials is non-linear and much stronger, so that it is easily observed, for instance, in the attraction between a refrigerator magnet and the iron of the refrigerator itself (Platonis Opera et al., 1839).

2.4 Ferromagnetism

Ferromagnetism is the basic mechanism by which certain materials (such as iron) form permanent magnets, or are attracted to magnets. In physics, several different types of magnetism are distinguished. Ferromagnetism (along with the similar effect ferrimagnetism) is the strongest type and is responsible for the common phenomena of magnetism in magnets encountered in everyday life. Substances respond weakly to magnetic fields with three other types of magnetism, Paramagnetism, diamagnetism, and Antiferromagnetism, but the forces are usually so weak that they can only be detected by sensitive instruments in a laboratory. An everyday example of ferromagnetism is a refrigerator magnet used to hold notes on a refrigerator door. The attraction between a magnet and ferromagnetic material is "the quality of magnetism first apparent to the ancient world, and to us today".

Permanent magnets (materials that can be magnetized by an external magnetic field and remain magnetized after the external field is removed) are either ferromagnetic or ferrimagnetic, as are the materials that are noticeably attracted to them. Only a few substances are ferromagnetic. The common ones are iron, nickel, cobalt and most of their alloys, and some compounds of rare earth metals. Ferromagnetism is very important in industry and modern technology, and is the basis for many electrical and

electromechanical devices such as electromagnets, electric motors, generators, transformers, and magnetic storage such as tape recorders, and hard disks, and nondestructive testing of ferrous materials (Fowler et al., 1997).

2.5 Antiferromagnetism

In materials that exhibit Antiferromagnetism, the magnetic moments of atoms or molecules, usually related to the spins of electrons, align in a regular pattern with neighboring spins (on different sublattices) pointing in opposite directions figure(2.2). This is, like ferromagnetism and ferrimagnetisms, a manifestation of ordered magnetism. Generally, Antiferromagnetic order may exist at sufficiently low temperatures, but vanishes at and above the Néel temperature – named after Louis Néel, who had first identified this type of magnetic ordering. Above the Néel temperature, the material is typically paramagnetic (Kumar Goyal,Rajendra, 2017).

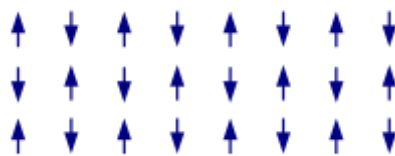


Figure (2.2): Antiferromagnetic Ordering

2.6 Ferrimagnetism

In physics, a ferrimagnetic material is one that has populations of atoms with opposing magnetic moments, as in Antiferromagnetism; however, in ferrimagnetic materials, the opposing moments are unequal

and a spontaneous magnetization remains figure(2.3). This happens when the populations consist of different materials or ions (such as Fe^{2+} and Fe^{3+}). Ferrimagnetism is exhibited by ferrites and magnetic garnets. The oldest known magnetic substance, magnetite (iron(II,III) oxide; Fe_3O_4), is a ferrimagnet; it was originally classified as a ferromagnetic before Néel's discovery of ferrimagnetism and antiferromagnetism in 1948(Shu-hua, 1954) Known ferrimagnetic materials include YIG (yttrium iron garnet), cubic ferrites composed of iron oxides and other elements such as aluminum, cobalt, nickel, manganese and zinc, hexagonal ferrites such as $\text{PbFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$, and pyrrhotite, Fe_{1-x}S (Li, Shu-hua, 1954) .

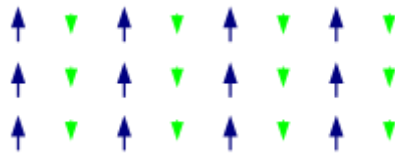


Figure (2.3): Ferrimagnetic Ordering

Chapter Three

Construction and Application

3.1 Introduction

In this chapter is the explanation of construction and the applications of each of classes' of magnetic materials.

3.2 Diamagnetism

Diamagnetism is a property of all materials, and always makes a weak contribution to the material's response to a magnetic field. However, other forms of magnetism (such as ferromagnetism or Paramagnetism) are so much stronger that when multiple different forms of magnetism are present in a material, the diamagnetic contribution is usually negligible. Substances where the diamagnetic behavior is the strongest effect are termed diamagnetic materials, or diamagnet. Diamagnetic materials are those that laypeople generally think of as non-magnetic, and include water, wood, most organic compounds such as petroleum and some plastics, and many metals including copper, particularly the heavy ones with many core electrons, such as mercury, gold and bismuth. The magnetic susceptibility values of various molecular fragments are called Pascal's constants (Schmidl, Petra G., 1997) . Diamagnetic materials, like water, or water-based materials, have a relative magnetic permeability that is less than or equal to 1, and therefore a magnetic susceptibility less than or equal to 0, since susceptibility is defined as $\chi_v = \mu_v - 1$. This means that diamagnetic materials are repelled by magnetic fields. However, since diamagnetism is such a weak property, its effects are not observable in everyday life. For example, the magnetic susceptibility of diamagnets such as water is $\chi_v = -9.05 \times 10^{-6}$. The most strongly diamagnetic material is bismuth, $\chi_v = -1.66 \times 10^{-4}$, although pyrolytic carbon may have a susceptibility of $\chi_v =$

-4.00×10^{-4} in one plane. Nevertheless, these values are orders of magnitude smaller than the magnetism exhibited by paramagnets and ferromagnets. Note that because χ_v is derived from the ratio of the internal magnetic field to the applied field, it is a dimensionless value (Einstein, 1905). All conductors exhibit an effective diamagnetism when they experience a changing magnetic field. The Lorentz force on electrons causes them to circulate around forming eddy currents. The eddy currents then produce an induced magnetic field opposite the applied field, resisting the conductor's motion (Meyers, 1997).

In rare cases, the diamagnetic contribution can be stronger than paramagnetic contribution. As is the case for gold, which has a magnetic susceptibility less than 0, so is by definition a diamagnetic material, but when measured carefully with X-ray magnetic circular dichroism, shows in table(3.1) an extremely weak paramagnetic contribution that is overcome by a stronger diamagnetic contribution (Catherine et al., 1998).

Table (3.1): Notable diamagnetic materials

| Notable diamagnetic materials (Du Tremolet de Lacheisserie et al., 2005) | |
|--|--|
| Material | $\chi_v [\times 10^{-5} \text{ (SI units)}]$ |
| Superconductor | -10^5 |
| Pyrolytic carbon | -40.9 |
| Bismuth | -16.6 |
| Mercury | -2.9 |
| Silver | -2.6 |
| Carbon (diamond) | -2.1 |
| Lead | -1.8 |
| Carbon (graphite) | -1.6 |
| Copper | -1.0 |
| Water | -0.91 |

3.3 Superconductor

Superconductors may be considered perfect diamagnets ($\chi_v = -1$), because they expel all magnetic fields (except in a thin surface layer) due to the Meissner effect see figure(3.1) (Du Tremolet de Lacheisserie et al., 2005).

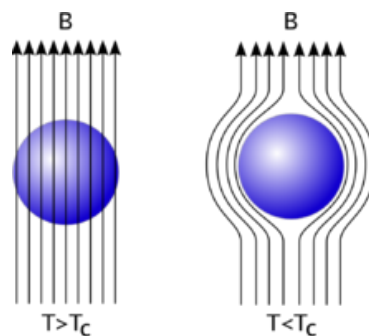


Figure (3.1): Transition from ordinary conductivity (left) to superconductivity (right). At the transition, the superconductor expels the magnetic field and then acts as a perfect diamagnet.

3.4 Demonstrations

Curving water surfaces

If a powerful magnet (such as a super magnet) is covered with a layer of water (that is thin compared to the diameter of the magnet) then the field of the magnet significantly repels the water. This causes a slight dimple in the water's surface that may be seen by its reflection see table (3.2) (Du Tremolet de Lacheisserie et al., 2005).

Table (3.2): Material Vs Curie temp (K)

| Material | Curie temp. (K) |
|---|-----------------|
| Co | 1388 |
| Fe | 1043 |
| Fe ₂ O ₃ | 948 |
| FeOFe ₂ O ₃ | 858 |
| NiOFe ₂ O ₃ | 858 |
| CuOFe ₂ O ₃ | 728 |
| MgOFe ₂ O ₃ | 713 |
| MnBi | 630 |
| Ni | 627 |
| MnSb | 587 |
| MnOFe ₂ O ₃ | 573 |
| Y ₃ Fe ₅ O ₁₂ ^[a] | 560 |
| CrO ₂ | 386 |
| MnAs | 318 |
| Gd | 292 |
| Tb | 219 |
| Dy | 88 |
| EuO | 69 |

3.5 Levitation

Diamagnets may be levitated in stable equilibrium in a magnetic field, with no power consumption. Earnshaw's theorem seems to preclude the possibility of static magnetic levitation. However, Earnshaw's theorem applies only to objects with positive susceptibilities, such as ferromagnets (which have a permanent positive moment) and paramagnets (which

induce a positive moment). These are attracted to field maxima, which do not exist in free space. Diamagnets (which induce a negative moment) are attracted to field minima, and there can be a field minimum in free space.

A thin slice of pyrolytic graphite, which is an unusually strong diamagnetic material, can be stably floated in a magnetic field, such as that from rare earth permanent magnets. This can be done with all components at room temperature, making a visually effective demonstration of diamagnetism. The Radboud University Nijmegen, the Netherlands, has conducted experiments where water and other substances were successfully levitated. Most spectacularly, a live frog figure(3.2) was levitated (Joseph et al., 1992).In September 2009, NASA's Jet Propulsion Laboratory (JPL) in Pasadena, California announced it had successfully levitated mice using a superconducting magnet, (Catherine et al., 1998) an important step forward since mice are closer biologically to humans than frogs (Purcell, 2012).JPL said it hopes to perform experiments regarding the effects of microgravity on bone and muscle mass. Recent experiments studying the growth of protein crystals have led to a technique using powerful magnets to allow growth in ways that counteract Earth's gravity (Merzouki,Rochdi et al., 2012).A simple homemade device for demonstration can be constructed out of bismuth plates and a few permanent magnets that levitate a permanent magnet (Sturgeon, 1825).



Figure (3.2): A live frog levitates inside a 32 mm (1.26 in) diameter vertical bore of a Bitter solenoid in a magnetic field of about 16 teslas at the Nijmegen High Field Magnet Laboratory (Du Tremolet de Lacheisserie et al., 2005).

3.6 Theory

The electrons in a material generally settle in orbitals, with effectively zero resistance and act like current loops. Thus it might be imagined that diamagnetism effects in general would be common, since any applied magnetic field would generate currents in these loops that would oppose the change, in a similar way to superconductors, which are essentially perfect diamagnets. However, since the electrons are rigidly held in orbitals by the charge of the protons and are further constrained by the Pauli exclusion principle, many materials exhibit diamagnetism, but typically respond very little to the applied field. The Bohr–van Leeuwen theorem proves that there cannot be any diamagnetism or paramagnetism in a purely classical system. However, the classical theory of Langevin for diamagnetism gives the same prediction as the quantum theory (Griffiths, 1998) The classical theory is given below.

3.7 Langevin Diamagnetism

Paul Langevin's theory of diamagnetism (1905) (Jackson, 1999) applies to materials containing atoms with closed shells. A field with intensity B , applied to an electron with charge e and mass m , gives rise to Larmor precession with frequency

$\omega = eB / 2m$. The number of revolutions per unit time is $\omega / 2\pi$, so the current for an atom with Z electrons is (in SI units) (Milton, Kmball, 2006).

$$I = \frac{-Ze^2B}{4\pi m} \quad (3.1)$$

The magnetic moment of a current loop is equal to the current times the area of the loop. Suppose the field is aligned with the z axis. The average loop area can be given as $\pi\langle\rho^2\rangle$, where $\langle\rho^2\rangle$ is the mean square distance of the electrons perpendicular to the z axis. The magnetic moment is therefore

$$\mu = -\frac{Ze^2B}{4m}\langle\rho^2\rangle \quad (3.2)$$

If the distribution of charge is spherically symmetric, we can suppose that the distribution of x, y, z coordinates are independent and identically distributed. Then $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = 1/3\langle r^2 \rangle$, where $\langle r^2 \rangle$ is the mean square distance of the electrons from the nucleus. Therefore $\langle\rho^2\rangle = \langle x^2 \rangle + \langle y^2 \rangle = \frac{2}{3}\langle r^2 \rangle$. If η is the number of atoms per unit volume, the volume diamagnetic susceptibility in SI units is

$$\chi = \frac{\mu_0 \eta \mu}{B} = -\frac{\mu_0 e^2 z \eta}{6m} \langle r^2 \rangle \quad (3.3)$$

3.8 In metals

The Langevin theory is not the full picture for metals because there are also non-localized electrons. The theory that describes diamagnetism in a free electron gas is called Landau diamagnetism, named after Lev Landau, (Guth, 1997) and instead considers the weak counteracting field that forms when the electrons' trajectories are curved due to the Lorentz force. Landau diamagnetism, however, should be contrasted with Pauli Paramagnetism, an effect associated with the polarization of delocalized

electrons' spins (Feynman, 2011; Feynman, 2011). For the bulk case of a 3D system and low magnetic fields, the (volume) diamagnetic susceptibility can be calculated using Landau quantization, which in SI units is

$$\chi = -\mu_0 \frac{e^2}{12\pi m\hbar^2} \sqrt{2mE_f} \quad (3.4)$$

where E_f is the Fermi energy. This is equivalent to $-\frac{\mu_0 \mu_B^2}{3} g(E_f)$ exactly-1/3 times Pauli paramagnetic susceptibility, where $\mu_B = \frac{e\hbar}{2m}$ is the Bohr magneton and $g(E)$ is the density of states (number of states per energy per volume). This formula takes into account the spin degeneracy of the carriers (spin $\frac{1}{2}$ electrons).

In doped semiconductors the ratio between Landau and Pauli susceptibilities may change due to the effective mass of the charge carriers differing from the electron mass in vacuum, increasing the diamagnetic contribution. The formula presented here only applies for the bulk; in confined systems like quantum dots, the description is altered due (Mills, 1993; Kirschvink, Joseph et al., 1992) to quantum confinement. Additionally, for strong magnetic fields, the susceptibility of delocalized electrons oscillates as a function of the field strength, a phenomenon known as the de Haas–van Alphen effect, also first described theoretically by Landau, (Guth, 1997).

3.9 Application

Because diamagnetism is essentially the expelling of magnetic fields within a material, strong diamagnetic materials can be levitated, or if they are sufficiently strong and enough area, can levitate magnets. Figure (3.3) shows a levitating piece of graphite. In the case of superconductors (Figure (3.4)), the diamagnetic response leaves no internal magnetic field. These

materials can be easily levitated in the presence of a strong permanent magnet as seen in Figure (3.3). However, high temperature superconductors (~ 100 K (Edward, 2001)) are made from exotic materials with expensive processing routes and require cryogenic fluids to accomplish the superconducting state (Feynman, 2011).

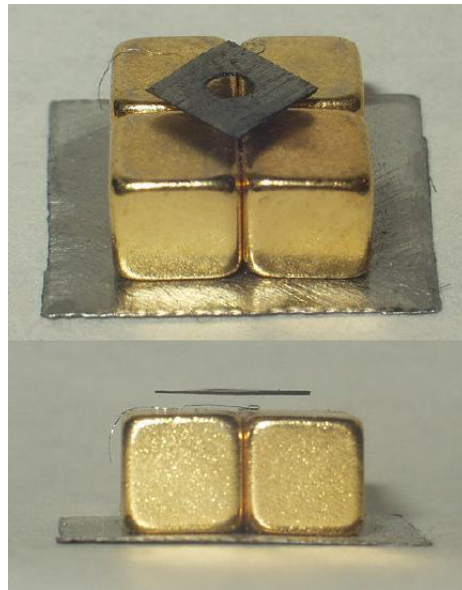


Figure (3.3): Diamagnetic levitation of pyrolytic graphite over permanent neodymium magnets (David K. Cheng, 1992).

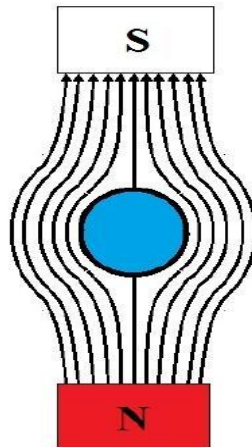


Figure (3.4): A superconductor (blue) expels all of its external magnetic field. They are perfect diamagnets.

3.10 Paramagnetism

Relation to electron spins

Constituent atoms or molecules of paramagnetic materials have permanent magnetic moments (dipoles), even in the absence of an applied field. The permanent moment generally is due to the spin of unpaired electrons in atomic or molecular electron orbitals (see Magnetic moment). In pure paramagnetism, the dipoles do not interact with one another and are randomly oriented in the absence of an external field due to thermal agitation, resulting in zero net magnetic moment. When a magnetic field is applied, the dipoles will tend to align with the applied field, resulting in a net magnetic moment in the direction of the applied field. In the classical description, this alignment can be understood to occur due to a torque being provided on the magnetic moments by an applied field, which tries to align the dipoles parallel to the applied field. However, the true origins of the alignment can only be understood via the quantum-mechanical properties of spin and angular momentum (Feynman, 2011). If there is sufficient energy exchange between neighbouring dipoles, they will interact, and may spontaneously align or anti-align and form magnetic domains, resulting in ferromagnetism (permanent magnets) or antiferromagnetism, respectively. Paramagnetic behavior can also be observed in ferromagnetic materials that are above their Curie temperature, and in antiferromagnets above their Néel temperature. At these temperatures, the available thermal energy simply overcomes the interaction energy between the spins. In general, paramagnetic effects are quite small: the magnetic susceptibility is of the order of 10^{-3} to 10^{-5} for most paramagnets, but may be as high as 10^{-1} for synthetic paramagnets such as ferrofluids (Mills, 1993).

3.11 Delocalization

In conductive materials, the electrons are delocalized, that is, they travel through the solid more or less as free electrons. Conductivity can be understood in a band structure picture as arising from the incomplete filling of energy bands. In an ordinary nonmagnetic conductor the conduction band is identical for both spin-up and spin-down electrons. When a magnetic field is applied, the conduction band splits apart into a spin-up and a spin-down band due to the difference in magnetic potential energy for spin-up and spin-down electrons. Since the Fermi level must be identical for both bands, this means that there will be a small surplus of the type of spin in the band that moved downwards. This effect is a weak form of Paramagnetism known as Pauli Paramagnetism (Joseph et al., 1992) see table (3.3). The effect always competes with a diamagnetic response of opposite sign due to all the core electrons of the atoms. Stronger forms of magnetism usually require localized rather than itinerant electrons. However, in some cases a band structure can result in which there are two delocalized sub-bands with states of opposite spins that have different energies. If one subband is preferentially filled over the other, one can have itinerant ferromagnetic order. This situation usually only occurs in relatively narrow (d-)bands, which are poorly delocalized (David K. Cheng, 1992).

Table (3.3): Selected Pauli-paramagnetic metals, (Joseph et al., 1992)

| Material | Magnetic susceptibility, (10^{-5}) (SI units) |
|-----------------|---|
| Tungsten | 6.8 |
| Caesium | 5.1 |
| Aluminium | 2.2 |
| Lithium | 1.4 |
| Magnesium | 1.2 |
| Sodium | 0.72 |

3.12 s and p electrons

Generally, strong delocalization in a solid due to large overlap with neighboring wave functions means that there will be a large Fermi velocity; this means that the number of electrons in a band is less sensitive to shifts in that band's energy, implying a weak magnetism. This is why s- and p-type metals are typically either Pauli-paramagnetic or as in the case of gold even diamagnetic. In the latter case the diamagnetic contribution from the closed shell inner electrons simply wins over the weak paramagnetic term of the almost free electrons (Edward, 2001).

3.13 d and f electrons

Stronger magnetic effects are typically only observed when d or f electrons are involved. Particularly the latter are usually strongly localized. Moreover, the size of the magnetic moment on a lanthanide atom can be quite large as it can carry up to 7 unpaired electrons in the case of gadolinium(III) (hence its use in MRI). The high magnetic moments associated with lanthanides is one reason why superstrong magnets are typically based on elements like neodymium or samarium (Edward, 2001).

3.14 Molecular localization

The picture in figure (3.5) is a generalization as it pertains to materials with an extended lattice rather than a molecular structure. Molecular structure can also lead to localization of electrons. Although there are usually energetic reasons why a molecular structure results such that it does not exhibit partly filled orbitals (i.e. unpaired spins), some non-closed shell moieties do occur in nature. Molecular oxygen is a good example. Even in the frozen solid it contains di-radical molecules resulting in paramagnetic behavior. The unpaired spins reside in orbitals derived from oxygen p wave functions, but the overlap is limited to the one neighbor in the O₂ molecules. The distances to other oxygen atoms in the lattice remain too large to lead to delocalization and the magnetic moments remain unpaired (David , 1998).



Figure (3.5): When liquid oxygen is poured from a beaker into a strong magnet, the oxygen is temporarily contained between the magnetic poles owing to its paramagnetism.

3.15 Theory

The Bohr–van Leeuwen theorem proves that there cannot be any diamagnetism or paramagnetism in a purely classical system. The

paramagnetic response has then two possible quantum origins, either coming from permanent magnetic moments of the ions or from the spatial motion of the conduction electrons inside the material. Both descriptions are given below (Helmut, 2007).

3.16 Curie's Law

For low levels of magnetization, the magnetization of paramagnets follows what is known as Curie's law, at least approximately. This law indicates that the susceptibility, χ , of paramagnetic materials is inversely proportional to their temperature, i.e. that materials become more magnetic at lower temperatures. The mathematical expression is (Edward, 2012):

$$M = \chi H = \frac{C}{T} H \quad (3.5)$$

Where:

M is the resulting magnetization, measured in amperes/meter (A/m),

χ is the volume magnetic susceptibility (dimensionless),

H is the auxiliary magnetic field (A/m),

T is absolute temperature, measured in Kelvin's (K),

C is a material-specific Curie constant (K).

Curie's law is valid under the commonly encountered conditions of low magnetization ($\mu_B H \leq k_B T$), but does not apply in the high-field/low-temperature regime where saturation of magnetization occurs ($\mu_B H \geq k_B T$) and magnetic dipoles are all aligned with the applied field. When the dipoles are aligned, increasing the external field will not increase the total magnetization since there can be no further alignment (Tipler, 2004). For a paramagnetic ion with noninteracting magnetic moments with angular

momentum J , the Curie constant is related the individual ions' magnetic moments,

$$C = \frac{\eta}{3K_B} \mu_{\text{eff}}^2 \quad \text{Where } \mu_{\text{eff}} = g J \mu_B \sqrt{J(J+1)} \quad (3.6)$$

where η is the number of atoms per unit volume. The parameter μ_{eff} is interpreted as the effective magnetic moment per paramagnetic ion. If one uses a classical treatment with molecular magnetic moments represented as discrete magnetic dipoles, μ , a Curie Law expression of the same form will emerge with μ appearing in place of μ_{eff} .

When orbital angular momentum contributions to the magnetic moment are small, as occurs for most organic radicals or for octahedral transition metal complexes with d^3 or high-spin d^5 configurations, the effective magnetic moment takes the form (with g -factor $g_e = 2.0023... \approx 2$),

$$\mu_{\text{eff}} \approx 2\sqrt{S(S+1)}\mu_B = \sqrt{N_u(N_u+2)}\mu_B \quad (3.7)$$

where N_u is the number of unpaired electrons. In other transition metal complexes this yields a useful, if somewhat cruder, estimate (Charles, 2007).

3.17 Pauli Paramagnetism

For some alkali metals and noble metals, conduction electrons are weakly interacting and delocalized in space forming a Fermi gas. For these materials one contribution to the magnetic response comes from the interaction between the electron spins and the magnetic field known as Pauli Paramagnetism. For a small magnetic field H , the additional energy per electron from the interaction between an electron spin and the magnetic field is given by (Basore, 1980):

$$\Delta E = -\mu_0 H, \mu_e \neq \mu_0 H. \left(-g e \frac{\mu_B}{h'} S \right) = \pm \mu_0 \mu_B H, \quad (3.8)$$

where μ_0 is the vacuum permeability, μ_e is the electron magnetic moment, μ_B is the Bohr magneton, h is the reduced Planck constant, and the g -factor cancels with the spin $S = \pm h'/2$. The \pm indicates that the sign is positive (negative) when the electron spin component in the direction of his parallel (antiparallel) to the magnetic field. For low temperatures with respect to the Fermi temperature (around 10^4 kelvins for metals), the number density of electrons $\eta^\uparrow(\eta^\downarrow)$ pointing parallel (antiparallel) to the magnetic field can be written as:

$$\eta^\uparrow \approx \frac{\eta^e}{2} - \frac{\mu_0 \mu_B}{2} g(E_f) H; \left(\eta^\downarrow \approx \frac{\eta^e}{2} + \frac{\mu_0 \mu_B}{2} g(E_f) H \right), \quad (3.9)$$

with η^e the total free-electrons density and $g(E_f)$ the electronic density of states (number of states per energy per volume) at the Fermi energy. In this approximation the magnetization is given as the magnetic moment of one electron times the difference in densities:

$$M = \mu_B (\eta^\downarrow - \eta^\uparrow) = \mu_0 \mu_B^2 g(E_f) H, \quad (3.10)$$

which yields a positive paramagnetic susceptibility independent of temperature:

$$\chi_p = \mu_0 \mu_B^2 g(E_f). \quad (3.11)$$

The Pauli paramagnetic susceptibility is a macroscopic effect and has to be contrasted with Landau diamagnetic susceptibility which is equal to minus one third of Pauli's and also comes from delocalized electrons. The Pauli susceptibility comes from the spin interaction with the magnetic field while the Landau susceptibility comes from the spatial motion of the electrons and it is independent of the spin. In doped semiconductors the ratio between Landau's and Pauli's susceptibilities changes as the effective mass of the charge carriers m^* can differ from the electron mass m_e .

The magnetic response calculated for a gas of electrons is not the full picture as the magnetic susceptibility coming from the ions has to be included. Additionally, these formulas may break down for confined systems that differ from the bulk, like quantum dots, or for high fields, as demonstrated in the de Haas-van Alphen effect. Pauli Paramagnetism is named after the physicist Wolfgang Pauli. Before Pauli's theory, the lack of a strong Curie Paramagnetism in metals was an open problem as the leading model could not account for this contribution without the use of quantum statistics (Murakami, 2000).

3.18 Examples of Paramagnets

Materials that are called "paramagnets" are most often those that exhibit, at least over an appreciable temperature range, magnetic susceptibilities that adhere to the Curie or Curie–Weiss laws. In principle any system that contains atoms, ions, or molecules with unpaired spins can be called a paramagnet, but the interactions between them need to be carefully considered (Bender, 2000).

3.19 Systems with Minimal Interactions

The narrowest definition would be: a system with unpaired spins that do not interact with each other. In this narrowest sense, the only pure paramagnet is a dilute gas of monatomic hydrogen atoms. Each atom has one non-interacting unpaired electron. The latter could be said about a gas of lithium atoms but these already possess two paired core electrons that produce a diamagnetic response of opposite sign. Strictly speaking Li is a mixed system therefore, although admittedly the diamagnetic component is weak and often neglected. In the case of heavier elements the diamagnetic contribution becomes more important and in the case of metallic gold it dominates the properties. The element hydrogen is virtually

never called 'paramagnetic' because the monatomic gas is stable only at extremely high temperature; H atoms combine to form molecular H₂ and in so doing, the magnetic moments are lost (quenched), because of the spins pair. Hydrogen is therefore diamagnetic and the same holds true for many other elements. Although the electronic configuration of the individual atoms (and ions) of most elements contain unpaired spins, they are not necessarily paramagnetic, because at ambient temperature quenching is very much the rule rather than the exception. The quenching tendency is weakest for f-electrons because *f* (especially 4f) orbitals are radially contracted and they overlap only weakly with orbitals on adjacent atoms. Consequently, the lanthanide elements with incompletely filled 4f-orbitals are paramagnetic or magnetically ordered (Moser et al., 2002).

Table (3.4): μ_{eff} values for typical d³ and d⁵ transition metal complexes (Moser et al., 2002).

| Material | $\mu_{\text{eff}}/\mu_{\text{B}}$ |
|---|-----------------------------------|
| [Cr(NH ₃) ₆]Br ₃ | 3.77 |
| [Cr(NH ₃) ₆]Br ₃ | 3.87 |
| [Cr(NH ₃) ₆]Br ₃ | 3.79 |
| K ₄ [V(CN) ₆] | 3.78 |
| K ₄ [V(CN) ₆] | 5.92 |
| K ₄ [V(CN) ₆] | 5.92 |
| NH ₄ [Fe(SO ₄) ₂]·12H ₂ O | 5.89 |

Thus, condensed phase paramagnets are only possible if the interactions of the spins that lead either to quenching or to ordering are kept at bay by structural isolation of the magnetic centers. There are two classes of materials for which this holds (Filatov et al., 2006).

- Molecular materials with a (isolated) paramagnetic center.
 - Good examples are coordination complexes of d- or f-metals or proteins with such centers, e.g. myoglobin. In such

materials the organic part of the molecule acts as an envelope shielding the spins from their neighbors.

- Small molecules can be stable in radical form, oxygen O_2 is a good example. Such systems are quite rare because they tend to be rather reactive.
- Dilute systems.
 - Dissolving a paramagnetic species in a diamagnetic lattice at small concentrations, e.g. Nd^{3+} in $CaCl_2$ will separate the neodymium ions at large enough distances that they do not interact. Such systems are of prime importance for what can be considered the most sensitive method to study paramagnetic systems: EPR.

3.20 Systems with Interactions

As stated below, many materials that contain d- or f-elements do retain unquenched spins. Salts of such elements often show paramagnetic behavior but at low enough temperatures the magnetic moments may order. It is not uncommon to call such materials 'paramagnets', when referring to their paramagnetic behavior above their Curie or Néel-points, particularly if such temperatures are very low or have never been properly measured.

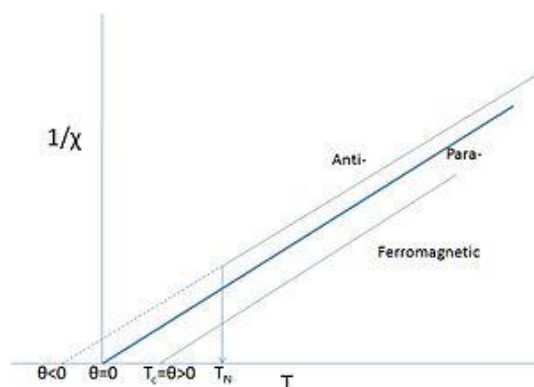


Figure (3.6): Idealized Curie–Weiss behavior; N.B. $T_C=0$, but T_N is not θ . Paramagnetic regimes are denoted by solid lines. Close to T_N or T_C the behavior usually deviates from ideal.

Even for iron it is not uncommon to say that iron becomes a paramagnet above its relatively high Curie-point. In that case the Curie-point is seen as a phase transition between a ferromagnet and a 'paramagnet'. The word paramagnet now merely refers to the linear response of the system to an applied field, the temperature dependence of which requires an amended version of Curie's law, known as the Curie–Weiss law:

$$M = \frac{C}{T-\theta} H \quad (3.12)$$

This amended law includes a term θ that describes the exchange interaction that is present albeit overcome by thermal motion. The sign of θ depends on whether ferro-or antiferromagnetic interactions dominate and it is seldom exactly zero, except in the dilute, isolated cases mentioned earlier.

Obviously, the paramagnetic Curie–Weiss description above T_N or T_C is a rather different interpretation of the word "paramagnet" as it does *not* imply the absence of interactions, but rather that the magnetic structure is random in the absence of an external field at these sufficiently high temperatures. Even if θ is close to zero this does not mean that there are no interactions, just that the aligning ferro- and the anti-aligning antiferromagnetic ones cancel. An additional complication is that the interactions are often different in different directions of the crystalline lattice (anisotropy), leading to complicated magnetic structures once ordered. Randomness of the structure also applies to the many metals that show a net paramagnetic response over a broad temperature range. They do not follow a Curie type law as function of temperature however, often they are more or less temperature independent. This type of behavior is of an itinerant nature and better called Pauli-paramagnetism, but it is not unusual to see, for example, the metal aluminium called a "paramagnet", even though interactions are strong enough to give this element very good electrical conductivity (Sandtner and Bleuler, 2004).

3.21 Super paramagnets

Some materials show induced magnetic behavior that follows a Curie type law but with exceptionally large values for the Curie constants. These materials are known as super paramagnets. They are characterized by a strong ferromagnetic or ferrimagnetic type of coupling into domains of a limited size that behave independently from one another. The bulk properties of such a system resemble that of a paramagnet, but on a microscopic level they are ordered. The materials do show an ordering temperature above which the behavior reverts to ordinary Paramagnetism (with interaction). Ferrofluids are a good example, but the phenomenon can also occur inside solids, e.g., when dilute paramagnetic centers are introduced in a strong itinerant medium of ferromagnetic coupling such as when Fe is substituted in TlCu_2Se_2 or the alloy AuFe. Such systems contain ferromagnetically coupled clusters that freeze out at lower temperatures. They are also called micromagnets (Sandtner and Bleuler, 2004).

3.22 Application

Paramagnetism is a form of magnetism whereby the paramagnetic material is only attracted when in the presence of an externally applied magnetic field. Paramagnetic materials have a relative magnetic permeability greater or equal to unity (i.e., a positive magnetic susceptibility) and hence are attracted to magnetic fields. The magnetic moment induced by the applied field is linear in the field strength; it is also rather weak.

Constituent atoms or molecules of paramagnetic materials have permanent magnetic moments (dipoles), even in the absence of an applied field. Generally, the permanent moment is caused by the spin of unpaired electrons in atomic or molecular electron orbitals. In pure Paramagnetism,

the dipoles do not interact with each other and are randomly oriented in the absence of an external field due to thermal agitation; this results in a zero net magnetic moment. When a magnetic field is applied, the dipoles will tend to align with the applied field, resulting in a net magnetic moment in the direction of the applied field (Amati et al., 2008).

Paramagnetic materials have a small, positive susceptibility to magnetic fields. These materials are slightly attracted by a magnetic field and the material does not retain the magnetic properties when the external field is removed, as illustrated in. Paramagnetic properties are due to the presence of some unpaired electrons, and from the realignment of the electron paths caused by the external magnetic field. Paramagnetic materials include magnesium, molybdenum, lithium and tantalum. Unlike ferromagnets, paramagnets do not retain any magnetization in the absence of an externally applied magnetic field, because thermal motion randomizes the spin orientations responsible for magnetism. Some paramagnetic materials retain spin disorder at absolute zero (meaning they are paramagnetic in the ground state). Thus the total magnetization drops to zero when the applied field is removed. Even in the presence of the field there is only a small induced magnetization because only a small fraction of the spins will be oriented by the field (Kluysken, 2007) see figure (3.7).

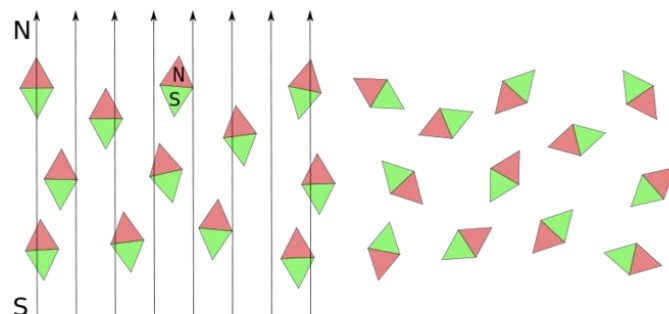


Figure (3.7): Paramagnetic Materials and Electric Fields: Orientation in paramagnetic material when electric field is applied (right image) and removed (left image).

3.23 Ferromagnetism

The table (3.5) below lists a selection of ferromagnetic and ferrimagnetic compounds, along with the temperature above which they cease to exhibit spontaneous magnetization (see Curie temperature). Ferromagnetism is a property not just of the chemical make-up of a material, but of its crystalline structure and microstructure. There are ferromagnetic metal alloys whose constituents are not themselves ferromagnetic, called Heusler alloys, named after Fritz Heusler. Conversely there are non-magnetic alloys, such as types of stainless steel, composed almost exclusively of ferromagnetic metals. Amorphous (non-crystalline) ferromagnetic metallic alloys can be made by very rapid quenching (cooling) of a liquid alloy. These have the advantage that their properties are nearly isotropic (not aligned along a crystal axis); this results in low coercivity, low hysteresis loss, high permeability, and high electrical resistivity. One such typical material is a transition metal-metalloid alloy, made from about 80% transition metal (usually Fe, Co, or Ni) and a metalloid component (B, C, Si, P, or Al) that lowers the melting point (Kluyskens, 2009), (Beams, 1954). A relatively new class of exceptionally strong ferromagnetic materials are the rare-earth magnets. They contain lanthanide elements that are known for their ability to carry large magnetic moments in well-localized f-orbitals.

Most ferromagnetic materials are metals, since the conducting electrons are often responsible for mediating the ferromagnetic interactions. It is therefore a challenge to develop ferromagnetic insulators, especially multiferroic materials, which are both ferromagnetic and ferroelectric (Beams, 1964).

Table (3.5): Curie temperatures for some crystalline ferromagnetic materials (Beams, 1964).

| Material | Curie temp. (K) |
|--|-----------------|
| Co | 1388 |
| Fe | 1043 |
| Fe ₂ O ₃ | 948 |
| FeOFe ₂ O ₃ | 858 |
| NiOFe ₂ O ₃ | 858 |
| CuOFe ₂ O ₃ | 728 |
| MgOFe ₂ O ₃ | 713 |
| MnBi | 630 |
| Ni | 627 |
| MnSb | 587 |
| MnOFe ₂ O ₃ | 573 |
| Y ₃ Fe ₅ O ₁₂ | 560 |
| CrO ₂ | 386 |
| MnAs | 318 |
| Gd | 292 |
| Tb | 219 |
| Dy | 88 |
| EuO | 69 |

3.24 Actinide Ferromagnets

A number of actinide compounds are Ferromagnets at room temperature or exhibit ferromagnetism upon cooling. PuP is a paramagnet with cubic symmetry at room temperature, but which undergoes a structural transition into a tetragonal state with ferromagnetic order when cooled below its $T_C = 125$ K. In its ferromagnetic state, PuP's easy axis is in the $\langle 100 \rangle$ direction (Habermann, H. et al., 1979).

In NpFe₂ the easy axis is $\langle 111 \rangle$. Above $T_C \approx 500$ K NpFe₂ is also paramagnetic and cubic. Cooling below the Curie temperature produces a rhombohedra distortion wherein the rhombohedra angle changes from 60° (cubic phase) to 60.53°. An alternate description of this distortion is to consider the length c along the unique trinomial axis (after the distortion

has begun) and a as the distance in the plane perpendicular to c . In the cubic phase this reduces to $c/a = 1.00$. Below the Curie temperature

$$\frac{c}{a} - 1 = -(120 \pm 5) * 10^{-4} \quad (3.13)$$

which is the largest strain in any actinide compound. NpNi_2 undergoes a similar lattice distortion below $T_C = 32$ K, with a strain of $(43 \pm 5) \times 10^{-4}$ (Moser et al., 2002) NpCo_2 is a ferrimagnet below 15 K (Habermann, H. et al., 1979).

3.25 Explanation

The Bohr–van Leeuwen theorem, discovered in the 1910s, showed that classical physics theories are unable to account for any form of magnetism, including ferromagnetism. Magnetism is now regarded as a purely quantum mechanical effect. Ferromagnetism arises due to two effects from quantum mechanics: spin and the Pauli Exclusion Principle (Schweitzer, 1976).

3.26 Origin of Magnetism

One of the fundamental properties of an electron (besides that it carries charge) is that it has a magnetic dipole moment, i.e., it behaves like a tiny magnet, producing a magnetic field. This dipole moment comes from the more fundamental property of the electron that it has quantum mechanical spin. Due to its quantum nature, the spin of the electron can be in one of only two states; with the magnetic field either pointing "up" or "down" (for any choice of up and down). The spin of the electrons in atoms is the main source of ferromagnetism, although there is also a contribution from the orbital angular of the electron about the nucleus. When these magnetic dipoles in a piece of matter are aligned, (point in the same

direction) their individually tiny magnetic fields add together to create a much larger macroscopic field. However, materials made of atoms with filled electron shells have a total dipole moment of zero, because the electrons all exist in pairs with opposite spin, every electron's magnetic moment is cancelled by the opposite moment of the second electron in the pair. Only atoms with partially filled shells (i.e., unpaired spins) can have a net magnetic moment, so ferromagnetism only occurs in materials with partially filled shells. Because of Hund's rules, the first few electrons in a shell tend to have the same spin, thereby increasing the total dipole moment. These unpaired dipoles (often called simply "spins" even though they also generally include orbital angular momentum) tend to align in parallel to an external magnetic field, an effect called Paramagnetism. Ferromagnetism involves an additional phenomenon, however: in a few substances the dipoles tend to align spontaneously, giving rise to a spontaneous magnetization, even when there is no applied field (Croot, 1987).

3.27 Exchange interaction

When two nearby atoms have unpaired electrons, whether the electron spins are parallel or antiparallel affects whether the electrons can share the same orbit as a result of the quantum mechanical effect called the exchange interaction. This in turn affects the electron location and the Coulomb (electrostatic) interaction and thus the energy difference between these states. The exchange interaction is related to the Pauli Exclusion Principle, which says that two electrons with the same spin cannot also be in the same spatial state (orbital). This is a consequence of the spin-statistics theorem and that electrons are fermions. Therefore, under certain conditions, when the orbitals of the unpaired outer valence electrons from adjacent atoms overlap, the distributions of their electric charge in space

are farther apart when the electrons have parallel spins than when they have opposite spins. This reduces the electrostatic energy of the electrons when their spins are parallel compared to their energy when the spins are antiparallel, so the parallel-spin state is more stable. In simple terms, the electrons, which repel one another, can move "further apart" by aligning their spins, so the spins of these electrons tend to line up. This difference in energy is called the exchange energy. This energy difference can be orders of magnitude larger than the energy differences associated with the magnetic dipole-dipole interaction due to dipole orientation, which tends to align the dipoles antiparallel. In certain doped semiconductor oxides RKKY interactions have been shown to bring about periodic longer-range magnetic interactions, a phenomenon of significance in the study of spintronic materials. The materials in which the exchange interaction is much stronger than the competing dipole-dipole interaction are frequently called magnetic materials. For instance, in iron (Fe) the exchange force is about 1000 times stronger than the dipole interaction. Therefore, below the Curie temperature virtually all of the dipoles in a ferromagnetic material will be aligned. In addition to ferromagnetism, the exchange interaction is also responsible for the other types of spontaneous ordering of atomic magnetic moments occurring in magnetic solids, antiferromagnetism and ferrimagnetism. There are different exchange interaction mechanisms which create the magnetism in different ferromagnetic, ferrimagnetic, and antiferromagnetic substances. These mechanisms include direct exchange, RKKY exchange, double exchange, and superexchange (Kasarda, 2000).

3.28 Magnetic Anisotropy

Although the exchange interaction keeps spins aligned, it does not align them in a particular direction. Without magnetic anisotropy, the spins in a magnet randomly change direction in response to thermal fluctuations

and the magnet is super paramagnetic. There are several kinds of magnetic anisotropy, the most common of which is magneto crystalline anisotropy. This is a dependence of the energy on the direction of magnetization relative to the crystallographic lattice. Another common source of anisotropy, inverse magnetostriction, is induced by internal strains. Single-domain magnets also can have shape anisotropy due to the magnetostatic effects of the particle shape. As the temperature of a magnet increases, the anisotropy tends to decrease, and there is often a blocking temperature at which a transition to super Paramagnetism occurs (Meeks, 1974).

3.29 Magnetic Domain

The above would seem to suggest that every piece of ferromagnetic material should have a strong magnetic field, since all the spins are aligned, yet iron and other ferromagnets are often found in an "unmagnetized" state. The reason for this is that a bulk piece of ferromagnetic material is divided into tiny regions called magnetic domains (also known as Weiss domains). Within each domain, the spins are aligned, but (if the bulk material is in its lowest energy configuration; i.e. unmagnetized), the spins of separate domains point in different directions and their magnetic fields cancel out, so the object has no net large scale magnetic field (Li,Xiaojun et al., 2018). Ferromagnetic materials spontaneously divide into magnetic domains because the exchange interaction is a short-range force, so over long distances of many atoms the tendency of the magnetic dipoles to reduce their energy by orienting in opposite directions wins out. If all the dipoles in a piece of ferromagnetic material are aligned parallel, it creates a large magnetic field extending into the space around it. This contains a lot of magnetostatic energy. The material can reduce this energy by splitting into many domains pointing in different directions, so the magnetic field is

confined to small local fields in the material, reducing the volume of the field. The domains are separated by thin domain walls a number of molecules thick, in which the direction of magnetization of the dipoles rotates smoothly from one domain's direction to the other (Smart, 2008).

3.30 Magnetized Materials

Thus, a piece of iron in its lowest energy state ("unmagnetized") generally has little or no net magnetic field. However, the magnetic domains in a material are not fixed in place; they are simply regions where the spins of the electrons have aligned spontaneously due to their magnetic fields, and thus can be altered by an external magnetic field. If a strong enough external magnetic field is applied to the material, the domain walls will move by the process of the spins of the electrons in atoms near the wall in one domain turning under the influence of the external field to face in the same direction as the electrons in the other domain, thus reorienting the domains so more of the dipoles are aligned with the external field. The domains will remain aligned when the external field is removed, creating a magnetic field of their own extending into the space around the material, thus creating a "permanent" magnet. The domains do not go back to their original minimum energy configuration when the field is removed because the domain walls tend to become 'pinned' or 'snagged' on defects in the crystal lattice, preserving their parallel orientation. This is shown by the Barkhausen effect: as the magnetizing field is changed, the magnetization changes in thousands of tiny discontinuous jumps as the domain walls suddenly "snap" past defects (Hoshi, H et al., 2006). This magnetization as a function of the external field is described by a hysteresis curve. Although this state of aligned domains found in a piece of magnetized ferromagnetic material is not a minimal-energy configuration, it is metastable, and can persist for long periods, as shown by samples of magnetite from the sea

floor which have maintained their magnetization for millions of years. Heating and then cooling (annealing) a magnetized material, subjecting it to vibration by hammering it, or applying a rapidly oscillating magnetic field from a degaussing coil tends to release the domain walls from their pinned state, and the domain boundaries tend to move back to a lower energy configuration with less external magnetic field, thus demagnetizing the material (Biological Systems - Heart Assist Pump). Commercial magnets are made of "hard" ferromagnetic or ferrimagnetic materials with very large magnetic anisotropy such as alnico and ferrites, which have a very strong tendency for the magnetization to be pointed along one axis of the crystal, the "easy axis". During manufacture the materials are subjected to various metallurgical processes in a powerful magnetic field, which aligns the crystal grains so, their "easy" axes of magnetization all point in the same direction. Thus the magnetization, and the resulting magnetic field, is "built in" to the crystal structure of the material, making it very difficult to demagnetize (Lembke, 2005).

3.31 Curie Temperature

As the temperature increases, thermal motion, or entropy, competes with the ferromagnetic tendency for dipoles to align. When the temperature rises beyond a certain point, called the Curie temperature, there is a second-order phase transition and the system can no longer maintain a spontaneous magnetization, so its ability to be magnetized or attracted to a magnet disappears, although it still responds paramagnetically to an external field. Below that temperature, there is a spontaneous symmetry breaking and magnetic moments become aligned with their neighbors. The Curie temperature itself is a critical point, where the magnetic susceptibility is theoretically infinite and, although there is no net magnetization, domain-like spin correlations fluctuate at all length scales.

The study of ferromagnetic phase transitions, especially via the simplified Ising spin model, had an important impact on the development of statistical physics. There, it was first clearly shown that mean field theory approaches failed to predict the correct behavior at the critical point (which was found to fall under a universality class that includes many other systems, such as liquid-gas transitions), and had to be replaced by renormalization group theory (Lembke, 2004).

3.32 Application

The most common ferromagnetic materials are cobalt, iron, nickel, along with Lodestone a naturally magnetized mineral and other rare earth metal compounds. A common usages of ferromagnetic materials affecting our everyday lives is through magnetic storage in the form of data. Otherwise considered non-volatile storage since data cannot be lost when the device it is not powered. An advantage of this storage method is that it is one of the cheaper forms of storing data, as well as having the ability to be re-used. This is all possible because of Hysteresis.

Once ferromagnetic materials are magnetized toward a specific direction it loses the ability to lose its magnetization (Hysteresis). Meaning it will not be able to go back to its original state without any magnetization. But another opposite magnetic field can be applied which would result in the creation of a hysteresis loop, as seen in figure (3.8). This ultimately is the unique effect that allows these materials to retain data, after the magnetizing field is dropped to zero (2010).

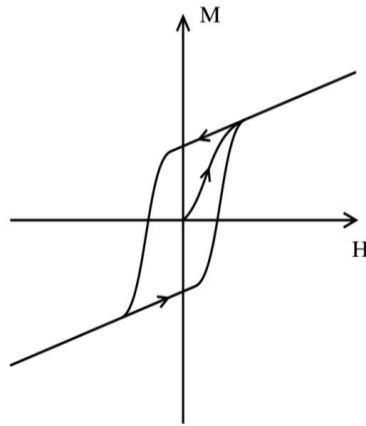


Figure (3.8) : Hysteresis loop for ferromagnetic material, depicts a decrease in the magnetic field (H) then an increase as it loops back to its initial starting point.

3.33 Anti-Ferromagnetism

Antiferromagnetic materials occur commonly among transition metal compounds, especially oxides. Examples include hematite, metals such as chromium, alloys such as iron manganese (FeMn), and oxides such as nickel oxide (NiO). There are also numerous examples among high nuclearity metal clusters. Organic molecules can also exhibit antiferromagnetic coupling under rare circumstances, as seen in radicals such as 5-dehydro-m-xylylene.

Antiferromagnets can couple to ferromagnets, for instance, through a mechanism known as exchange bias, in which the ferromagnetic film is either grown upon the antiferromagnet or annealed in an aligning magnetic field, causing the surface atoms of the ferromagnet to align with the surface atoms of the antiferromagnet. This provides the ability to "pin" the orientation of a ferromagnetic film, which provides one of the main uses in so-called spin valves, which are the basis of magnetic sensors including modern hard drive read heads. The temperature at or above which an antiferromagnetic layer loses its ability to "pin" the magnetization direction of an adjacent ferromagnetic layer is called the blocking temperature of

that layer and is usually lower than the Néel temperature (Amati et al., 2009).

3.34 Other Properties

Synthetic antiferromagnets (often abbreviated by SAF) are artificial antiferromagnets consisting of two or more thin ferromagnetic layers separated by a nonmagnetic layer. Dipole coupling of the ferromagnetic layers results in antiparallel alignment of the magnetization of the ferromagnets. Antiferromagnetism plays a crucial role in giant magnetoresistance, as had been discovered in 1988 by the Nobel prize winners Albert Fert and Peter Grünberg (awarded in 2007) using synthetic antiferromagnets. There are also examples of disordered materials (such as iron phosphate glasses) that become antiferromagnetic below their Néel temperature. These disordered networks 'frustrate' the antiparallelism of adjacent spins; i.e. it is not possible to construct a network where each spin is surrounded by opposite neighbour spins. It can only be determined that the average correlation of neighbour spins is antiferromagnetic. This type of magnetism is sometimes called speromagnetism. An interesting phenomenon occurs in anisotropic Heisenberg antiferromagnets in a field, where spin-flop and supersolid phases may be stabilized. The latter phase has been described first by Takeo Matsubara and H. Matsuda in 1956 (Filatov et al.).

3.35 Application

Antiferromagnets are very interesting in nature but do not have a wide range of applications as other magnetic materials do. This is due to their lack of spontaneous magnetization. However because their structural magnetization is closely related to ferrimagnets they can be used along with ferromagnets to test theoretical models used to explain

ferrimagnetism. The lack an overall magnetic moment which makes them suitable for providing magnetic reference points in magnetic sensors since the structure of antiferromagnets is not sensitive to external fields. A growing theory and source of research on Antiferromagnets is their contribution to superconductivity. There are materials that exhibit antiferromagnetic and ferromagnetic transition states. Their corresponding structural and magnetic properties transition resemble that of a metal-insulator transition and as a result there is a large change in conductivity with an applied field. Since most nonmetallic superconductors have antiferromagnetic phase, research continues to test antiferromagnets for sought after superconducting properties (Filatov,A. et al., 2002).

3.36 Ferrimagnetism

Unlike ferromagnetic materials, which are typically metals, ferrimagnetic materials are ceramics, in particular, ceramic oxides. The most widely used ferrimagnets in technological devices are materials known as ferrites. Ferrites are electrically insulating transitional-metal oxides with the general chemical formula $MO \cdot Fe_2 \cdot O_3$, where M is a divalent ion such as Mn^{2+} , Fe^{2+} , Co^{2+} , or Ni^{2+} . Ferrites are often prepared by standard ceramic processing techniques. In the case of $NiO \cdot Fe_2 \cdot O_3$ powders of NiO and Fe_2O_3 are mixed together and pressed into the desired shape before sintering (firing) at high temperature to form a dense ceramic of the desired composition. This method provides a reliable way of forming a wide variety of shapes and sizes of ferrimagnetic materials for embedding into technological devices (Basore, 1980).

3.37 Effect of Temperature

Ferrimagnetic materials are like ferromagnets in that they hold a spontaneous magnetization below the Curie temperature and show no

magnetic order (are paramagnetic) above this temperature. However, there is sometimes a temperature below the Curie temperature, at which the two opposing moments are equal, resulting in a net magnetic moment of zero; this is called the magnetization compensation point. This compensation point is observed easily in garnets and rare-earth–transition-metal alloys (RE-TM). Furthermore, ferrimagnets may also have an angular-momentum compensation point, at which the net angular momentum vanishes. This compensation point is a crucial point for achieving high speed magnetization reversal in magnetic memory devices (Sato M. a., 2000) see figure (3.9).

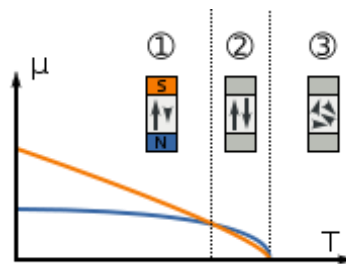


Figure (3.9): ① Below the magnetization compensation point, ferrimagnetic material is magnetic. ② At the compensation point, the magnetic components cancel each other and the total magnetic moment is zero. ③ Above the Curie point, the material loses magnetism.

3.38 Properties

Ferrimagnetic materials have high resistivity and have anisotropic properties. The anisotropy is actually induced by an external applied field. When this applied field aligns with the magnetic dipoles, it causes a net magnetic dipole moment and causes the magnetic dipoles to precess at a frequency controlled by the applied field, called Larmor or precession frequency. As a particular example, a microwave signal circularly polarized in the same direction as this precession strongly interacts with the magnetic dipole moments; when it is polarized in the opposite direction, the interaction is very low. When the interaction is strong, the

microwave signal can pass through the material. This directional property is used in the construction of microwave devices like isolators, circulators and gyrators. Ferrimagnetic materials are also used to produce optical isolators and circulators. Ferrimagnetic minerals in various rock types are used to study ancient geomagnetic properties of Earth and other planets. That field of study is known as pale magnetism (Post, 2000).

3.39 Molecular Ferrimagnets

Ferrimagnetism can also occur in molecular magnets. A classic example is a dodecanuclear manganesemolecule with an effective spin $S = 10$ derived from antiferromagnetic interaction on Mn(IV) metal centers with Mn(III) and Mn(II) metal centers (Moser R., et al., 2002).

3.40 Application

Ferrites have following application:

- Ferrites have importance in engineering and technology because they possess spontaneous magnetic moment below the Curie temperature just as iron, cobalt, nickel.
- Due to very low eddy current losses, ferrites are used as a core of coils in microwave frequency devices and computer memory core elements.
- Due to relatively low permeability and flux density compared to iron, ferrites are not suitable for the use in high field and high power applications, such as motors, generators and power transformers, but they can be used in low field and low power applications.
- Ferrites are used as ferromagnetic insulators in electrical circuits.
- Ferrites like ZnO find low frequency applications in timers. They are also used as switches in refrigerators, air conditioners, etc.
- Ferrites are used as magnetic head transducer in recording (Filatov et al., 2006).

Chapter Four

Conclusion and Recommendation

4.1 Conclusion

Magnetism and its classes is a class of physical phenomena that are mediated by magnetic fields. Electric currents and the magnetic moments of elementary particles give rise to a magnetic field, which acts on other currents and magnetic moments. The most familiar effects occur in ferromagnetic materials, which are strongly attracted by magnetic fields and can be magnetized to become permanent magnets, producing magnetic fields themselves. Only a few substances are ferromagnetic; the most common ones are iron, nickel and cobalt and their alloys such as steel. Although ferromagnetism is responsible for most of the effects of magnetism encountered in everyday life, all other materials are influenced to some extent by a magnetic field, by several other types of magnetism. Paramagnetic substances such as aluminum and oxygen are weakly attracted to an applied magnetic field; diamagnetic substances such as copper and carbon are weakly repelled; while Antiferromagnetic materials such as chromium and spin glasses have a more complex relationship with a magnetic field. The force of a magnet on paramagnetic, diamagnetic, and Antiferromagnetic materials is usually too weak to be felt, and can be detected only by laboratory instruments, so in everyday life these substances are often described as non-magnetic.

The magnetic state (or magnetic phase) of a material depends on temperature and other variables such as pressure and the applied magnetic field. A material may exhibit more than one form of magnetism as these variables change. As with magnetizing a magnet, demagnetizing a magnet is also possible. "Passing an alternate current, or hitting a heated magnet in an east west directions are ways of demagnetizing a magnet", quotes Sreekethav.

4.2 Recommendation

High magnetic field and its classes science is having an important impact in many disciplines, including medicine, chemistry, and condensed-matter physics. Recent accomplishments include the development of functional magnetic resonance imaging (fMRI), which is revolutionizing neuroscience; optically pumped magnetic resonance techniques, which allow visualization of new quantum phenomena in semiconductors; and ion cyclotron resonance mass spectroscopy, which is becoming an important tool for exploring the chemical composition of complex systems. High-field research has led to the discovery of new states of matter in low-dimensional systems, and it has also provided the first indications of how high-temperature superconductors evolve into unconventional metallic alloys in the extreme quantum limit. Improvements in ancillary instrumentation and the development of new strategies for using high-field magnets have contributed to these advances and should continue to do so. Outstanding work continues to be done in the area of magnet engineering, the discipline on which all these other activities depend. There are every reason to believe that developments as interesting as these will continue in the decades to come, especially if magnets are built that deliver higher fields than those available today. For instance, discoveries made using pulsed-field magnets, which operate at very high fields and are equipped with instruments that take full advantage of advances in electronics, could take research in fruitful new directions that cannot now be anticipated.

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