

# CHAPTER 9

## Magnetic Properties of Transition Metal Complexes:

### ❖ Elementary Theory of Magneto-Chemistry

The history of magnetism starts earlier than 600 B.C., but the initiation of conceptual understanding dates back only in the twentieth century, after which the scientific community started developing technologies based on this understanding. The phenomenon of magnetism was most likely first detected in the mineral magnetite, also called “lodestone ( $\text{Fe}_3\text{O}_4$ )”, which is essentially a chemical compound of iron and oxygen with inverse spinel structure. In ancient times, the Greeks were the first who used this compound and called it a magnet due to its remarkable capability to attract iron pieces or other blocks of the same material. Plato (428-348 B.C.) and Aristotle have also given some description of permanent magnets in their writings. The first record of a magnetic compass used for navigational purpose comes from a Chinese writing (1040 A.D.). The first systematic scientific investigation of the phenomenon of magnetism was carried out by a British physicist William Gilbert (1540-1603); who also discovered that the earth is also a weak magnet itself. A French military engineer and physicist Charles-Augustin de Coulomb (1736-1806) initiated the quantitative studies of magnetic phenomena in the eighteenth century. He gave the inverse square law, telling that the attraction force between two magnetic objects is directly proportional to the multiplication of their individual field strengths and inversely proportional to the square of their distance of separation. Danish physicist, H. C. Oersted (1777-1851), first proposed a link between the magnetism and electricity. French physicist Andre Marie Ampere (1775-1836) and British physicist Michael Faraday (1791-1869) carried out the experiments involving the effects of magnetic and electric fields on one another. Finally, the legendary Scotsman, James Clerk Maxwell (1831-1879), provided the theoretical basis to the physics of electromagnetism in the nineteenth century by showing that the magnetism and electricity are just the two faces of the same coin.

The modern point of view of magnetism in condensed matter originates from the work of two French physicists, Pierre Curie (1859-1906) and Pierre Weiss (1865-1940). Pierre Curie studied how the temperature affects magnetism of different materials and witnessed that magnetism vanished quickly above a certain critical temperature in materials like iron. Pierre Weiss put forward a theory about magnetism which was based upon the internal magnetic field, present at the molecular scale, which is proportional to the magnetic average that aligns the micro-magnets in magnetic substances. Today’s understanding of magnetic phenomena counts on the theory of the motion and interactions of electrons in atoms, given by Ernest Ising and Werner Heisenberg. The study of the magnetic field generated by the motion of electrons and nuclei in different materials help us to rationalize various fundamental effects and phenomenon. For example, nuclear magnetic resonance is one of the most important tools to characterize organic and inorganic compounds; or the study of magnetic properties of transition metal complexes has provided a beautiful insight of stereochemistry of metal centers and the nature of metal-ligand bonding. The branch of chemistry which is especially concerned with the magnetic properties of chemical compounds is generally called as magneto-chemistry.

➤ **Basic Terminology**

Now before we start to discuss the classical and quantum mechanical aspects of magneto-chemistry, some terms, which will be used very frequently, must be defined.

**1. Magnetic field strength ( $H$ ):** The magnetic fields produced by currents are calculated using Biot-Savart Law or Ampere's Law; and are generally measured in Tesla (T). However, when the fields so created pass through the magnetic things which can have magnetic fields induced internally; uncertainties can arise about which part of the field comes from the material considered and which part of the field comes from the external currents. Therefore, it is a common practice to distinguish the two by defining another magnetic field quantity " $H$ " usually called as "magnetic field strength". Thus, the magnetic field strength ( $H$ ) is one of two ways that can be used to express the magnetic field intensity. To be precise, a distinction is made between magnetic flux density  $B$ , measured in Newton per ampere-meter (N/mA), also called tesla (T) and magnetic field strength  $H$ , measured in amperes per meter (A/m).

**2. Magnetic induction ( $B$ ):** The phenomenon of the rise of magnetism in a specimen of magnetic material when it is placed in an external magnetic field is called as magnetic induction. The term "magnetic induction" is sometimes also referred as "magnetic flux density" which may be defined as the total number of magnetic lines of force crossing a unit area around a point positioned inside an object placed in the magnetizing field. The generally used symbol for magnetic induction or magnetic flux density is " $B$ "; and the relationship between total magnetic flux ( $\phi$ ) and magnetic flux density is  $B = \phi/a$ , where  $a$  is the cross-sectional area in square meter. The SI unit for magnetic flux density is the Tesla (T) which is equal to Weber/m<sup>2</sup> or N/mA.

**3. Magnetic permeability ( $\mu$ ):** The magnetic permeability, or simply the permeability, may be defined as the relative decrease or increase in the total magnetic-field inside a substance compared to the magnetizing field, the given material placed within. In other words, the permeability of a material is equal to the magnetic flux density ( $B$ ) created within the material by a magnetizing field divided by the intensity of magnetizing field i.e. magnetic field strength ( $H$ ). Therefore, magnetic permeability is defined as  $\mu = B/H$ . In SI units, permeability is measured in Henry per meter (H/m), or equivalently in Newton (kg m/s<sup>2</sup>) per ampere squared (NA<sup>-2</sup>).

**4. Intensity of magnetization ( $I$ ):** The intensity of magnetization represents the extent up to which a material has been magnetized under the influence of the magnetizing field. The intensity of magnetization of a magnetic material is thus defined as the magnetic moment per unit volume of the material i.e.  $I = M/V$ , where  $M$  is the magnetic moment which is equal to the product of pole strength and the distance of separation of magnetic poles of the specimen. Like  $H$ , the intensity of magnetization is also measured in amperes per meter (A/m).

**5. Magnetic susceptibility ( $K$ ,  $\chi$ ,  $\chi_M$ ):** The magnetic susceptibility is simply a measure of the magnetic properties of a material. The magnetic susceptibility shows whether a substance is repelled out or attracted into a magnetic field, which in turn has practical applications. Mathematically, volume susceptibility ( $K$ ) is the ratio of the intensity of magnetization to the applied magnetizing field intensity i.e.  $K = I/H$ . Now because the units of  $I$  and  $H$  are same, volume susceptibility is a dimensionless quantity. However, volume susceptibility divided by the density of the material is called as mass susceptibility ( $\chi$ ) which is measured in cm<sup>3</sup> g<sup>-1</sup>. The  $\chi$  multiplied by molar mass is called as molar susceptibility ( $\chi_M$ ) which is measured in cm<sup>3</sup> mol<sup>-1</sup>.

➤ **The Classical Concept of Magnetism**

The classical theory of magnetism was developed long before quantum mechanics. The Lenz's law states that when a substance is placed within a magnetic field of strength  $H$ , the field-induced within the substance ( $B$ ) differs from  $H$  by  $4\pi I$  i.e. the difference is proportional to the intensity of magnetization of the material. Mathematically, we can state this relationship as:

$$B = H + 4\pi I \quad (1)$$

Dividing equation (1) throughout by  $H$ , we get

$$\frac{B}{H} = 1 + 4\pi \frac{I}{H} \quad (2)$$

Now putting the value of  $I/H = K$  (volume susceptibility) in equation (2), we get

$$\frac{B}{H} = 1 + 4\pi K \quad \text{or} \quad 4\pi K = \frac{B}{H} - 1 \quad (3)$$

For some materials, the ratio of  $B/H$  is less than one, which means the value of  $K$  is negative, these materials are labeled as diamagnetic materials. For some materials, the ratio of  $B/H$  is greater than one, which means the value of  $K$  is positive, these materials are labeled as paramagnetic materials. The mass susceptibility ( $\chi$ ) in  $\text{cm}^3 \text{g}^{-1}$  can be obtained as:

$$\chi = \frac{K}{d} \quad (4)$$

Or the molar susceptibility in  $\text{cm}^3 \text{mol}^{-1}$  can be calculated from equation (4) as follows:

$$\chi_M = \chi \times M \quad (5)$$

Where  $d$  and  $M$  are the density and gram molar mass of the material, respectively. Since this value includes the underlying diamagnetism of paired electrons, it is necessary to correct for the diamagnetic portion of  $\chi_M$  to get a corrected paramagnetic susceptibility i.e. measured susceptibility ( $\chi_M$ ) = paramagnetic susceptibility ( $\chi_M^P$ ) + diamagnetic susceptibility ( $\chi_M^D$ ).

$$\chi_M^P = \chi_M - \chi_M^D \quad (6)$$

The values of these corrections are generally tabulated in the laboratory manuals and are available on-line too.

A French physicist, Pierre Curie, was investigating the effect of temperature on magnetic properties in the ending times of the nineteenth century. He discovered that, for a large number of paramagnetic substances, molar magnetic susceptibility ( $\chi_M$ ) varies inversely with the temperature. This observation is called as Curie law, which states that:

$$\chi_M \propto \frac{1}{T}$$

$$\chi_M = \frac{C}{T} \quad (7)$$

Where is  $C$  is the Curie constant having different magnitude for different substances. Curie also discovered that for every ferromagnetic substance, there is a temperature  $T_C$  above which, the normal paramagnetic behavior occurs. Later work by Onnes and Perrier showed that, for many paramagnetic substances, a more precise relationship is:

$$\chi_M = \frac{C}{T + \theta} \quad (8)$$

Where is  $\theta$  is the Weiss constant and the equation (8) is popularly known as the Curie-Weiss law. The symbol “ $\theta$ ” used in equation (8) is sometimes replaced by  $T_C$  because in the case of ferromagnetic materials, the value of  $\theta$  calculated by Curie-Weiss plot, is actually equal to the negative of their Curie temperature. That’s why there is another popular form of the Curie-Weiss law as given below.

$$\chi_M = \frac{C}{T - \theta} \quad (9)$$

The conventions shown in equation (8) are more widely accepted by the British and American academics, while the form with a negative sign is more popular in Indian and German universities. Furthermore, Louis Neel, another French physicist, observed that for every antiferromagnetic substance, there is a temperature  $T_N$  above which, the normal paramagnetic behavior occurs.

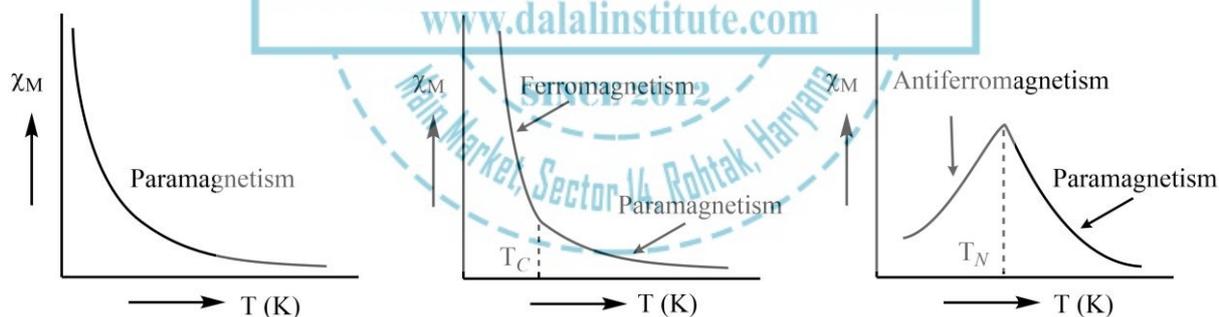


Figure 1. Plot of magnetic susceptibility vs temperature for normal paramagnetic, ferromagnetic and antiferromagnetic materials.

Normally, the reciprocal of magnetic susceptibility is plotted versus temperature ( $1/\chi_M$  vs  $T$  follows a straight line equation); which makes the use of both forms of Curie-Weiss law. The symbol “ $\theta$ ” in equation (9) is replaced by  $T_C$ , which gives suitable form for ferromagnetic substances (magnetic moments of atoms align to produce a strong magnetic effect); while the replacement of the symbol “ $\theta$ ” by  $T_N$  in equation (8) gives the suitable form for antiferromagnetic materials (magnetic moments of atoms align anti-parallel to produce a strong magnetic effect).

Therefore, for ferromagnetic substances

$$\chi_M = \frac{C}{T - T_C} \quad (10)$$

For antiferromagnetic substances

$$\chi_M = \frac{C}{T + T_N} \quad (11)$$

It is also worthy to mention that the normal paramagnetic behavior of ferromagnetic or antiferromagnetic materials is observed only when  $T > \theta$ .

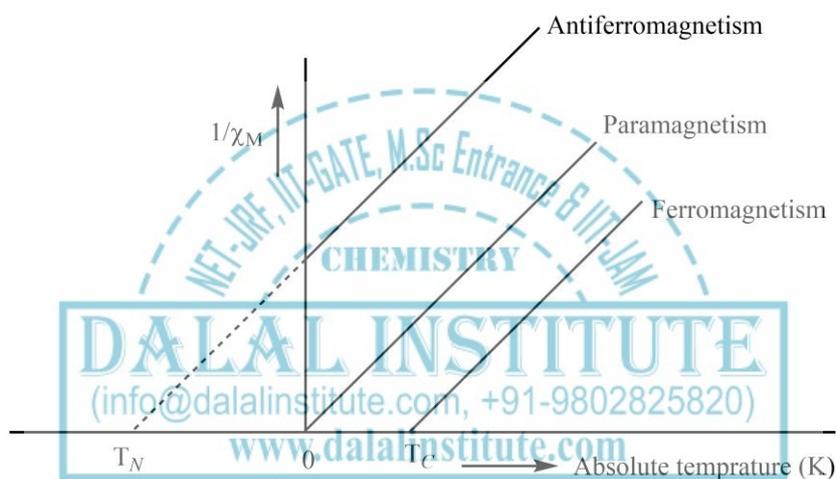


Figure 2. The plot of reciprocal of magnetic susceptibility vs temperature for normal paramagnetic, ferromagnetic and antiferromagnetic materials.

Thus, for ferromagnetic and antiferromagnetic materials, the value of  $\theta$  is generally labeled  $T_C$  (Curie temperature) and  $T_N$  (Neel temperature), respectively.

### ➤ *The Quantum Mechanical Concept of Magnetism*

The genesis of magnetic phenomena in all atoms lies in the orbital and spin motions of electrons and how these electrons interact with each other. The orbital motion of the electron gives rise to the orbital magnetic moment ( $\mu_l$ ), and the spin motion generates the spin magnetic moment ( $\mu_s$ ). The total magnetic moment of an atom is actually the resultant of the two aforementioned effects. Now, though the wave mechanical model of an atom is more precise in the rationalization of different atomic properties, the prewave mechanical model of an atom is still very much of use for understanding certain quantum mechanical effects. In the Bohr model, the electron is considered as a negatively charged hard-sphere that spins about its own axis as well as revolves around the positively charged heavy center of the atom. The pictorial representation of the rise of the magnetic moment by these two kinds of motion is shown below.

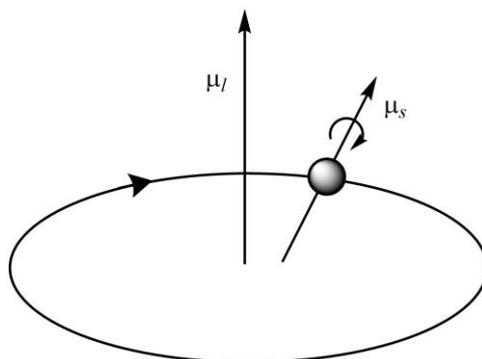


Figure 3. The generation of orbital magnetic moment ( $\mu_l$ ) and spin magnetic moment ( $\mu_s$ ) from prewave mechanical quantum theory.

Thus, we can agree on the fact that a more conceptual comprehensive understanding of the phenomena of magnetism in different chemical compounds requires us to start from the most elementary ideas of spin and orbital magnetic moments.

**1. Orbital magnetic moment ( $\mu_l$ ):** The motion of a negatively charged electron in a circular path is very much analogous to the current flowing through a ring of conducting material. Consequently, a magnetic field in a direction perpendicular to the plane of the ring or orbit is generated. The strength of the magnetic field thus produced can be obtained by multiplying the magnitude of the current flowing ( $i$ ) with the surface area of that ring ( $A$ ). Mathematically, the magnitude of the orbital magnetic moment ( $\mu_l$ ) can be given as:

$$\mu_l = iA = \left(\frac{e\omega}{2\pi c}\right)\pi r^2 \quad (12)$$

Where  $e$  is the electronic charge,  $\omega$  is the angular velocity of the electron,  $c$  is the velocity of light and  $r$  is the radius of the orbit. From the quantum theory of angular momentum, we know that the magnitude of the angular momenta of an orbiting electron is given by the following relation.

$$L_{\text{quantum mechanical}} = \sqrt{l(l+1)} \frac{h}{2\pi} \quad (13)$$

Where  $L$  is magnitude angular momentum due to orbital motion and  $l$  is the quantum number for the same. Moreover, the magnitude of angular momentum from classical mechanics is given by the product of angular velocity ( $\omega$ ) and moment of inertia ( $I$ ).

$$L_{\text{classical}} = I\omega \quad (14)$$

Putting  $I = mr^2$  in equation (14) we get

$$L_{\text{classical}} = mr^2\omega \quad (15)$$

Now, it is a well-known fact that all values of the quantum domain are also present in the classical domain though the vice-versa is not true. Therefore, we can put equation (13) equal to equation (15) to find the classical analogs.

$$mr^2\omega = \sqrt{l(l+1)} \frac{h}{2\pi} \quad (16)$$

Or

$$\omega r^2 = \sqrt{l(l+1)} \frac{h}{2\pi m} \quad (17)$$

Putting the value of  $\omega r^2$  from equation (17) into equation (12), we get

$$\mu_l = \frac{e}{2e} \left( \sqrt{l(l+1)} \frac{h}{2\pi m} \right) \quad (18)$$

$$\mu_l = \sqrt{l(l+1)} \left( \frac{eh}{4\pi mc} \right) \quad (19)$$

$$\mu_l = \sqrt{l(l+1)} \text{ B.M.} \quad (20)$$

Comparing equation (20) and equation (13), we can conclude that the magnitude of magnetic moment ( $\mu_l$ ) in the units of Bohr magneton (B.M.) is equal to orbital angular momentum (L) measured in the units of  $h/2\pi$ . It is also worthy to note that both the vectors ( $\mu_l$  and L) are collinear but oriented in the opposite direction. In other words, if the magnetic moment is oriented upward to the orbit plane, orbital angular momentum is downward, and vice-versa.

**2. Spin magnetic moment ( $\mu_s$ ):** In 1926, two American-Dutch physicists, named Samuel Goudsmit and George Uhlenbeck, observed that the angular momentum possessed by the moving electron is actually greater than the orbital angular momentum. This excess of angular momentum was then attributed to the spinning motion of the electron. This spinning motion of a negatively charged electron about its own axis is also analogs to the current-carrying circular conductor. Accordingly, a magnetic field, in a direction along to the spinning axis, is generated. They also postulated that the ratio of the spin magnetic moment ( $\mu_s$ ) measured in the units of B.M. to the spin angular momentum (S) measured in the units of  $h/2\pi$ , must be equal to 2. This ratio is called as Lande's splitting factor or the "g" value.

$$\frac{\mu_s}{S} = \frac{\mu_s}{\sqrt{s(s+1)}} = g \quad (21)$$

$$\mu_s = g\sqrt{s(s+1)} = 2\sqrt{s(s+1)} \text{ B.M.} \quad (22)$$

Where  $s$  is the quantum number defining the spin motion of the electron and  $[s(s+1)]^{1/2}$  is the corresponding spin angular momentum in the units of  $h/2\pi$  as discussed earlier.

Both types of magnetic moments will interact with the external magnetic field and will tend to align themselves along the direction of the field; which in turn will reinforce the magnitude of the applied field. In multi-electron systems, the spin motion of the individual electrons will interact with each other to give resultant spin motion quantum number “ $S$ ”; while the orbital motion of individual electrons will interact to give resultant orbital motion quantum number “ $L$ ”. Now, if  $L$  and  $S$  do not interact with each other, the overall magnetic moment will just be the sum of their individual magnetic moments. However, if the resultant spin and resultant orbital motions do couple, and the overall magnetic moment will be obtained from “ $J$ ” i.e. total angular momentum quantum number. The phenomena like diamagnetism, paramagnetism, or ferromagnetism arise as a result of alignments and interactions of these micro magnets.

➤ **Classes of Magnetic Materials**

The most primitive way to classify different materials on the basis of their magnetic properties is how they respond to the externally applied magnetic field. Thereafter, we can discuss the cause or interaction responsible for such behavior. In some material, the atomic-scale magnetic moments do not interact with each other; while in some cases the strong interaction may lead to a very complex magnetic profile depending upon the structural specificity. Different magnetic materials can be classified into the following four major classes:

**1. Diamagnetic materials:** When some substances are placed in an external magnetic field, the number of magnetic lines of force passing through the substance is less than the number of magnetic lines of force passing through the vacuum. This eventually means that the ratio of  $B/H$  is less than one, which gives a negative value of magnetic susceptibility ( $K$ ). Such substances are called as diamagnetic substances and are repelled by the external magnetic field.

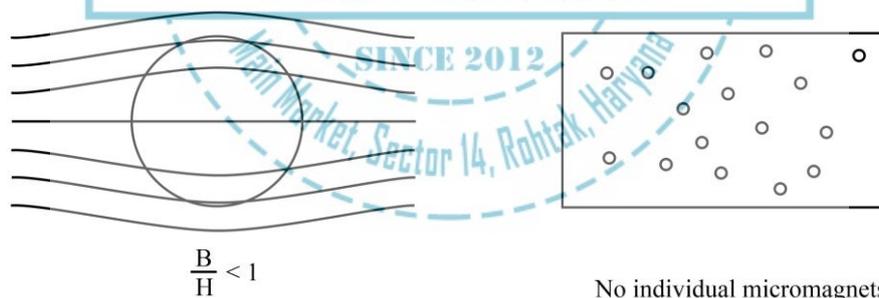


Figure 4. The behavior of a diamagnetic body in the externally applied magnetic field and corresponding magnetic domain.

Diamagnetic substances do not have unpaired electrons, and therefore the magnetic moment produced by one electron is canceled out by the other one. The phenomenon of diamagnetism is 1000 times weaker than paramagnetism, which makes it unobservable in substances with unpaired electrons. However, the measured magnetic susceptibilities must be corrected for the underlying diamagnetic effect, because most of the materials do contain paired electrons. Diamagnetic susceptibility is generally independent both of field strength and temperature.

**2. Paramagnetic materials:** When some substances are placed in an external magnetic field, the number of magnetic lines of force passing through the substance is more than the number of magnetic lines of force passing through the vacuum. This eventually means that the ratio of  $B/H$  is greater than one, which gives a positive value of magnetic susceptibility ( $K$ ). Such substances are called as paramagnetic substances and are attracted by the external magnetic field.

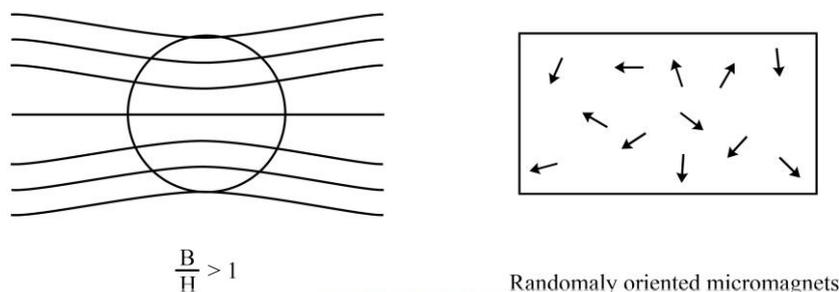


Figure 5. The behavior of a paramagnetic body in the externally applied magnetic field and corresponding magnetic domain.

Paramagnetic substances do have unpaired electrons, and therefore there is a net magnetic moment possessed by individual constituents. However, these micro-magnets are randomly oriented. The paramagnetic susceptibility of these materials decreases with the increase of temperature and follow simple Curie law. Hence, the paramagnetic susceptibility is generally independent of field strength, but markedly dependent on the temperature of the system.

**3. Ferromagnetic materials:** When some substances are placed in the external magnetic field, the number of magnetic lines of force passing through the substance is hugely greater than the number magnetic lines of force passing through the vacuum. This eventually means that the ratio of  $B/H$  is much greater than 1, which gives a positive value of magnetic susceptibility ( $K$ ) of order as high as  $10^4$ . Such substances are called as ferromagnetic substances and are strongly attracted by the external magnetic field.

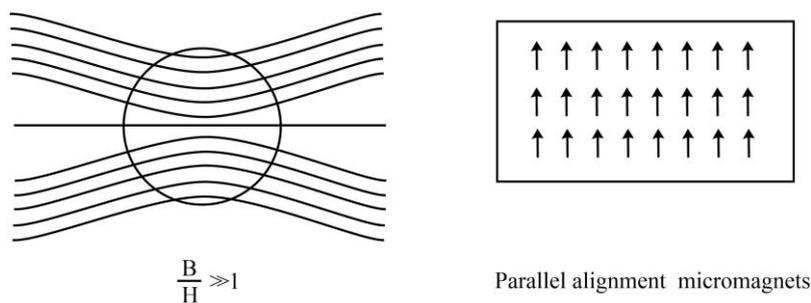


Figure 6. The behavior of a ferromagnetic body in an externally applied magnetic field and corresponding magnetic domain.

Ferromagnetic substances do have unpaired electrons, and therefore there is a net magnetic moment possessed by individual constituents. However, a special interaction of these micro-magnets makes them orient parallel to each other yielding very strong paramagnetism. The hysteresis and remanence and are characteristic features of ferromagnetic materials. Hence, the ferromagnetic susceptibility depends upon the field strength as well as the temperature of the system considered.

**4. Antiferromagnetic materials:** When some substances are placed in an external magnetic field, the number of magnetic lines of force passing through the substance is slightly greater than the number magnetic lines of force passing through the vacuum. This eventually means that the ratio of  $B/H$  is slightly greater than one, which gives a very small positive value of magnetic susceptibility ( $K$ ). Such substances are called as antiferromagnetic substance and are weakly attracted by the external magnetic field.

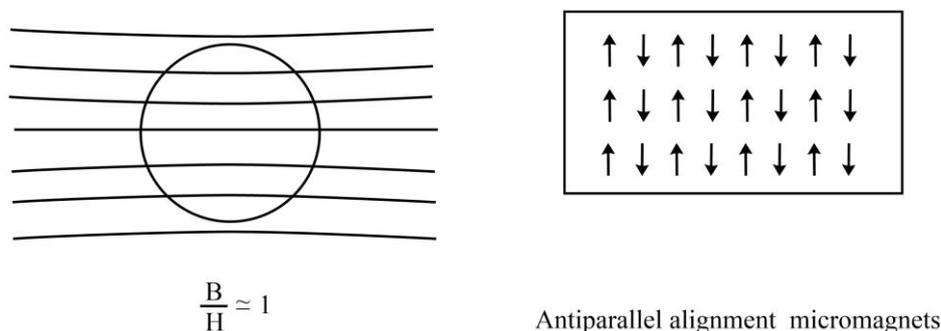


Figure 7. The behavior of an antiferromagnetic body in an externally applied magnetic field and corresponding magnetic domain.

Antiferromagnetic substances do have unpaired electrons, and therefore, are expected to show paramagnetism due to the presence of net magnetic moment possessed by individual constituents. However, a special interaction of these micro-magnets makes them orient antiparallel to each other yielding a very small value of positive magnetic susceptibility. The antiferromagnetic susceptibility usually depends on the temperature of the system only, though the dependence on field strength is also observed sometimes.

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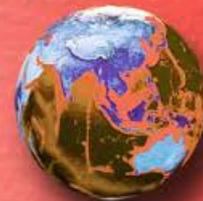
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