

PHYSICAL PRINCIPLES OF MAGNETISM

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The physical process of magnetism at the atomic level is described, where magnetic fields may be produced by both the orbital and spin motions of the electrons. This is then extended to molecules and crystalline metals and explains why the magnetic properties of ferromagnetic iron are so much different than those of say copper.

1. INTRODUCTION

Magnetisation at the atomic level is produced by both the orbital and spin motions of electrons. The large magnetic fields produced in ferromagnetic transition elements (Co, Ni, Fe) are mainly due to electron spin. These ferromagnetic materials are crystalline, and the atoms form cubic (or hexagonal) structures, in which the electrostatic forces lead to an alignment of electron spins in neighbouring atoms, and hence spontaneous magnetisation, up to saturation levels in one or more of the six easy directions, normal to the cube faces.

However this spontaneous magnetisation process does not of itself produce one large magnet out of a piece of ferromagnetic material, since it must also satisfy the condition of lowest energy level. Therefore instead of forming one large magnet, the material is spontaneously magnetised in a large number of magnetic domains. These domains are all magnetised to saturation levels but are in different directions so that the magnetic energy is minimised and the net magnetisation very small. The magnetic domains are separated by relatively thin regions (Bloch walls) over which the direction of magnetisation gradually changes. These Bloch walls require energy and equilibrium is reached when the energy saved by splitting a domain into two smaller ones with different directions is less than that required to establish the resulting Bloch wall.

When an external magnetic field is applied to a ferromagnetic material, the familiar magnetisation process consists of a movement of the domain walls so that those domains that have been spontaneously magnetised in the direction of the applied field grow at the expense of others which are opposed to the applied field, with a gradual reduction in the number of Bloch walls, so that eventually the material behaves

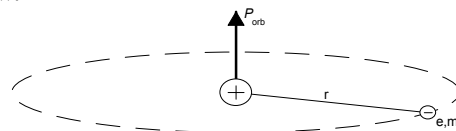
like one big domain and macroscopically is fully magnetised. Some Bloch wall movements are reversible while others are not, so that when the external magnetic field is removed it is the irreversible movements that give rise to hysteresis.

2. ATOMIC MAGNETISM

Ampere's hypothesis that minute circulating currents within a magnetic material are the source of magnetism is still relevant.

2.1 Hydrogen type atoms

In Bohr's theory, the electron revolves around the nucleus at such a velocity that the centrifugal force (mv^2/r) balances out the electrostatic force of attraction ($Ze^2/4\pi\epsilon_0 r^2$). The orbiting electron has angular momentum, which is an integral multiple of $h/2\pi$, where h is Planck's constant. The atomic number Z is equal to the total number of electrons in a particular atom and for hydrogen is unity, as shown below.



Orbital angular momentum

$$p_1 = m v r = n \left(\frac{h}{2\pi} \right) = n \hbar \dots\dots(1)$$

$$\text{Orbital velocity, } v_n = \frac{Ze^2}{2\epsilon_0 n h} = \frac{Z}{n} \frac{c}{1371}$$

and the corresponding frequency

$$f_n = \frac{v}{2\pi r} = \frac{Z^2}{n^3} \left(\frac{e^4 m}{4 h^3 \epsilon_0^2} \right) = \frac{Z^2}{n^3} 6.576 \times 10^{15} \text{ Hz}$$

2.1.1 Orbital Magnetic Moment

The orbiting electron acts like a current loop, with a magnetic moment ($\mu_l = i \times \text{Area}$). Orbital current

$$i = ef = \frac{Z^2}{n^3} \left(\frac{e^5 m}{4h^3 \epsilon_0^2} \right) = \frac{Z^2}{n^3} 1.05 \times 10^{-3} \text{ Amps}$$

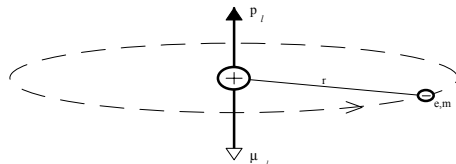
This acts like a magnet with a magnetic moment of

$$\mu_l = \mu_0 iA = \frac{\mu_0 e}{2m} p_l = \frac{\mu_0 e \hbar}{2m} = n \mu_B \dots \dots (2)$$

where the Bohr Magnetron is given by

$$\mu_B = \frac{e\hbar}{4\pi m} = 9.274 \times 10^{-24} \text{ J/T or Amp.m}^2$$

The magnetic moment (p_l) depends upon the area of the orbital and is independent of its shape. An electron in the first orbital ($n=1$), has a magnetic moment of 1 Bohr Magnetron (μ_B), due to its orbital motion round the nucleus.



From (1) and (2) it can be seen that the ratio of magnetic moment to angular momentum for orbital motion is independent of n , and is given by:

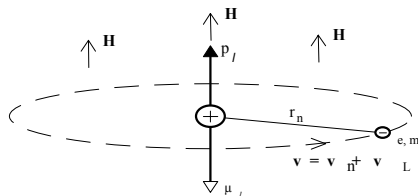
$$\frac{\mu_{orb}}{p_{orb}} = \frac{\mu_l}{p_l} = -\frac{\mu_0 e}{2m} \dots \dots (3)$$

2.2 Sommerfeld's Extensions of Bohr's Theory

Elliptical orbits were introduced into each shell so that for a given n , there are actually n different elliptical orbits. All ellipsoids at the n^{th} level have the same total energy, which is the same as that of Bohr's model, but each of the elliptical orbits have different angular momentum.

2.3 Larmor Precession

When an electron orbits around the nucleus in an applied magnetic field H , the radius of the orbit remains unaltered but the velocity of the electron changes as indicated below.



For the conditions shown above, the orbiting electron experiences an inward force (F_H) due to its motion in the magnetic field H .

$$F_H = ev \times B = ev \times \mu_0 H = ev \mu_0 H \approx ev_n \mu_0 H$$

Now the outwardly directed centrifugal force (mv^2/r) due to the motion of the electron around the nucleus, must balance the electrostatic force of attraction to the nucleus ($Ze^2/4\pi\epsilon_0 r^2$) plus the extra inward force F_H , due to the applied magnetic field H , so that

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2} + F_H, \text{ where } v = v_n + \Delta v$$

Thus the velocity of the electron has to increase by Δv , to compensate for the magnetic field.

$$\therefore \Delta v = \left(\frac{r}{2v_n m} \right) F_H = r \left(\frac{e}{2m} \right) \mu_0 H = v_L = \omega_L r$$

$$\therefore \text{Larmor Frequency, } \omega_L = \left(\frac{e\mu_0}{2m} \right) H = \frac{\mu_l}{p_l} H$$

If the electron had been orbiting in the other direction, its orbital magnetic moment (μ_l) would be in line with H , and its velocity reduced. Thus when an electron orbits in a magnetic field H , its velocity changes so as to oppose the applied field.

In the above discussion the plane of the orbiting electron was assumed to be normal to the magnetic field H . Due to space quantisation however this condition is not possible, and the electron orbit has to make an angle θ with the applied magnetic field H , the orbit itself precessing in the field H at the Larmor frequency, $\omega_L = (\mu_l/\mu_l) H$.

2.4 Electron Spin

The concept of electron spin explains the slightly different energy levels that electrons in the same orbit can take, and classically assumes that an electron is spinning in one of two opposite directions about its own axis with a spin quantum number of $\pm 1/2$.

Associated with this spin is an angular momentum (p_s), and a magnetic moment (μ_s). As e is a natural unit for charge, so is p_s for angular momentum.

$$\mu_s = \mp \frac{\mu_0 e \hbar}{4\pi m} = \mp \frac{\mu_0 e \hbar}{2m} = \mp \mu_B \dots \dots (4)$$

$$p_s = \pm \frac{\hbar}{4\pi} = \pm \frac{\hbar}{2} \dots \dots (5)$$

$$\text{Thus } \frac{\mu_s}{p_s} = \frac{e}{m} = 2 \frac{\mu_l}{p_l} \dots \dots (6)$$

3. QUANTUM THEORY

Bohr's theory and its extensions to include elliptical orbits and spins, as been superseded by quantum

mechanics where each electron in the atom is characterised by a set of 4 quantum numbers n, l, m , and s .

3.1 Principle Quantum Number (n)

Values (1, 2, 3,) related to the size and energy of the orbital. The energy difference between shells reduces with increasing n , due to electrons in the lower shells screening the nucleus.

3.2 Orbital Quantum Number (l)

Values of l from 0 to $(n - 1)$ are related to the shape and angular momentum of the orbits.

Orbital angular momentum of electron is

$$P_l = \hbar \sqrt{l(l+1)}, \text{ where } l = 0, 1, 2, \dots, (n-1)$$

with corresponding orbital magnetic moment

$$\mu_l = \frac{e\hbar}{2m} \sqrt{l(l+1)}, \text{ where } \hbar = \frac{h}{2\pi}$$

l values of 0, 1, 2, 3 are usually identified as subshells s, p, d, f respectively, and the energy between these subshells is relatively constant.

The zero angular momentum subshell s (ie. $l = 0$) corresponds to spherically symmetrical orbits. The energy of the orbitals increases slightly with l .

Shell	s	p	d	f
l	0	1	2	3
P_l	0	$\sqrt{2}$	$\sqrt{6}$	$\sqrt{12}$

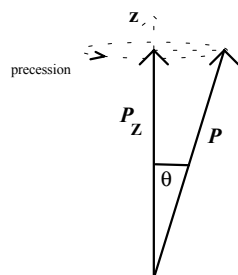
The magnetic moment of the orbiting electron is $\mu_l = (e/2m) p_l$ as given by (3).

3.3 Quantisation of angular momentum

Angular momentum of any object P is given by:

$$P = \hbar \sqrt{l(l+1)}$$

This angular momentum vector P can be considered to precess about an observed z direction of the vector. The projection P_z remaining constant (ie. sharp) while the components along the x and y axes time average to zero as indicated below.

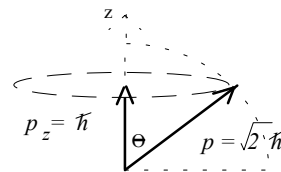


The component of P in the z direction is, $P_z = l\hbar$

For macroscopic objects the value of l is very large so $P_z \approx P$, and the quantisation is insignificant.

However for atomic electrons the max value of $l = (n-1)$, so that for example, in the second Bohr orbit of hydrogen

$$P_z = (n-1)\hbar = \hbar, \text{ \& } P = \sqrt{l(l+1)} \hbar = \sqrt{2} \hbar$$



3.4 Space quantisation of angular momentum

The angular momentum of an object, in any direction where it is sharp (eg. along the z axis), is quantised in units of \hbar so that

$$P_z = k\hbar, \text{ where } k = 0, \pm 1, \pm 2, \dots, \pm l.$$

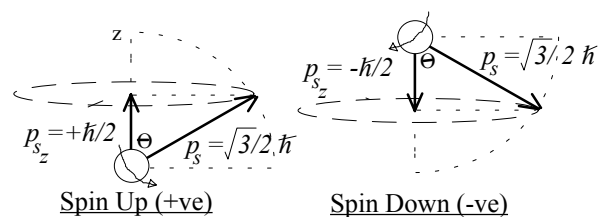
Since the projection of p onto the z axis is quantised, so too must be its orientation.

3.5 Spin quantum number (s)

Spin is an inherent, fixed property of every electron and produces an angular momentum

$$P_s = s\hbar, \text{ where } s = 1/2, \text{ \& } s^* = \sqrt{s(s+1)} = \sqrt{3}/2$$

Thus $P_s = \sqrt{3}/2 \hbar$ and it precesses around the z-axis with a value of $\pm \hbar/2$, as shown below.



This spin angular momentum (p_s) produces a corresponding magnetic moment (μ_s), and the ratio of spin magnetic moment to spin angular is double that due to orbital motion.

$$\mu_s / P_s = 2(\mu_0 e / 2m) \mu_B, \text{ so } \mu_s = 2s^* \mu_B = \sqrt{3} \mu_B$$

$$\text{and its projection on the z-axis is } \mu_{sz} = \pm \mu_B.$$

3.6 Magnetic quantum numbers m_l and m_s

These are associated with the quantisation of μ_l and μ_s along the direction of an applied magnetic field sufficiently strong to break down ls couplings.

$m_l = 0 \pm 1 \pm 2, \dots, \pm l$, and $m_s = \pm 1/2$
and the total $m = m_l + m_s$, $p = m\hbar$, $\mu = m\mu_B$

3.7 Total angular momentum of electron

In ls coupling, the orbital and spin angular momenta of an electron combine to form the total $p_j = j\hbar = \sqrt{j(j+1)}\hbar$, where $j = l \pm s = l \pm 1/2$.

The resultant magnetic moment is $\mu_j = jg\mu_B$, where the Lande factor

$$g = 1 + \left(\frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \right)$$

When $l=0$ the electron has spin only and $g=2$. In the hypothetical case of orbital motion with no spin $g=1$.

4. MAGNETIC MOMENT OF ATOMS

Electron states in atoms are grouped into orbitals, characterised by values of n and l . For a given value of l there are $2l+1$ possible states, each with a different magnetic quantum number, m_l . Each of these states has two possible values of spin m_s , and can be occupied by 2 electrons with opposite spin.

4.1 Energy Levels

The energy level of the shells increases with n . However, some levels in the 3d subshell have a higher energy level than those in the 4s, because the energy difference between consecutive shells becomes smaller and smaller with increasing n , while that between subshells is relatively constant. Thus the 4s shell will be filled before completing the 3d. A subshell is usually filled with the lower energy spin up electrons before being paired with electrons with spin down (Hund's rule), although there are exceptions.

The subshell energy levels are ordered as follows:

$$1s < 2s < 2p < 3s < 3p < 4s \approx 3d < 4p < 5s < 4d \dots$$

It can be seen that the $3d \approx 4s$ and that the 4d is greater than the 5s.

4.2 Total angular momentum of a free atom

The angular momentum and magnetic moment of all spherically symmetric shells (eg. full shells) sum to zero so we need only be concerned with shells that are partially full.

A method known as Russel-Saunders coupling or LS coupling is used to determine the combined angular momentum and magnetic moment of the electrons in the outermost subshells of an atom.

S , L , & J are the atomic counterparts of s , l , & j .

$$S = \sum m_s, \quad L = \sum m_l, \quad J = L + S$$

Spin magnetic moment of atom

$$\mu_S = 2S\mu_B, \text{ where } S = \sqrt{S(S+1)}$$

Orbital magnetic moment of atom

$$\mu_L = L\mu_B, \text{ where } L = \sqrt{L(L+1)}$$

Total magnetic moment of atom

$$\mu_J = Jg\mu_B, \text{ where } J = \sqrt{J(J+1)}$$

The magnetic moments μ_S and μ_L precess about the axis of J with resultant value μ_J .

4.3 Atomic magnetic moments of free atoms

(a) Hydrogen (1 electron)

$$l = ml = 0$$

$n=1$ ↑ Electron with Spin Up

$$S = +1/2, L = 0, J = 1/2, J^* = S^* = \sqrt{3}/2$$

$$\mu_L = 0, \mu_S = \sqrt{3}\mu_B, \mu_J = g\sqrt{3}/2\mu_B = \sqrt{3}\mu_B$$

This has only 1 electron and the most probable distance at which the electron can be found is on a spherical surface of radius 0.00529 nm. In this case the spherically symmetrical orbit produces zero orbital angular momentum.

(b) Oxygen (8 electrons)

		Angular Momentum #, l		
		0=s	1=p	
		0	Magnetic #, m	
Principle #, n	1	↑↓	↑	↓
	2	↑↓	↑	↑

$$S = 1, L = 1, J = 2, S^* = L^* = \sqrt{2}, J^* = \sqrt{6}$$

$$\mu_S = \sqrt{8}\mu_B, \mu_L = \sqrt{2}\mu_B, g = 1.5$$

$$\mu_J = g\sqrt{6}\mu_B = 1.5\sqrt{6}\mu_B = 3.67\mu_B$$

After filling the lower energy 1s and 2s shells with paired electrons having opposite spins, the 2p subshell is progressively filled with lower energy spin up electrons, before being paired with spin down. Thus the two outermost electrons in the oxygen atom are as shown above with spin up. The magnetic moments of the paired electrons in full shells cancel each other out, so that oxygen atoms have a spin magnetic moment of $\sqrt{8}\mu_B$, and a orbital magnetic moment of $\sqrt{2}\mu_B$.

Angular Momentum #. l

	0=s		1=p		2=d				
	0		1		2				
	<u>Magnetic #. m</u>								
1	↑↓	+1	0	-1					
2	↑↓	↑↓	↑↓	↑↓	+2	+1	0	-1	-2
3	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	↑
4	↑↓								

Principle #. n

$$S = 2, L = 2, J = 4, S^* = \sqrt{6}, L^* = \sqrt{6}, J^* = \sqrt{20},$$

$$\mu_S = \sqrt{12}\mu_B, \mu_L = \sqrt{6}\mu_B, g = 1.5$$

$$\mu_J = g\sqrt{20}\mu_B = 1.5\sqrt{20}\mu_B = 6.7\mu_B$$

Since the energy level of the 4s subshell is lower than some of the levels in the 3d, the 4s subshell is filled with paired electrons before the highest energy electrons go into 3d. However the 3d subshell is incomplete and the atom is left with a resultant magnetic moment of $\sqrt{12}\mu_B$ due to spin.

In its metallic form the average spin magnetic moment of iron is $2.2\mu_B$.

Angular Momentum #. l

	0=s	1=p	2=d
	0		
	<div>↑↓</div>		
		+1 0 -1	
1	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	
2	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	+2 +1 0 -1 -2
3	<div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div>	<div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div> <div>↑↓</div>
4	<div>↑</div>		

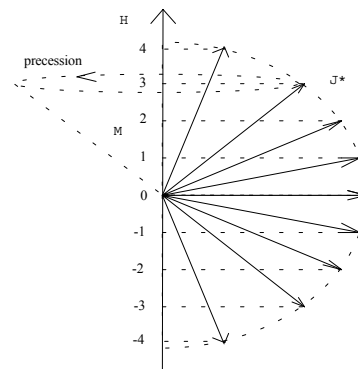
Principle #. n

The 3d shell in atomic copper is completely filled and so contributes nothing to the resultant magnetic moment. However there is a contribution due to the unpaired electron in the 4s subshell.

In its metallic form however the magnetic moment of copper is zero.

The vector J^* determines the resultant angular momentum and magnetic moment of a free atom. In the presence of a weak magnetic field H the vector J^* precesses about the direction of H such that the resolved value of J^* in the field direction is $M = 0, \pm 1, \pm 2, \pm 3, \dots, \pm J$. Space quantisation therefore limits J^* to take up one of $2J+1$ possible angular positions.

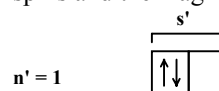
In the case of a free atom of iron $J = 4$, $J^* = \sqrt{20}$, and the 9 possible orientation of J^* are as follows.



The vector J^* actually precesses around H and cannot align itself exactly with H . The component of angular momentum in the direction of $H = m\hbar$, and the corresponding magnetic moment is $g\mu_B$.

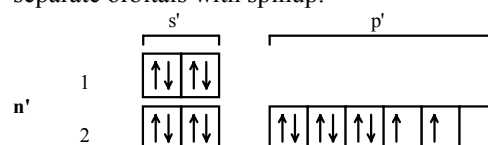
When two or more atoms come together to form a molecule, the inner electrons remain associated with their respective nuclei but the outer electrons belong to the molecule as a whole. The energy level of the outer orbitals are changed slightly (hybrid orbitals) to achieve minimum energy.

For example, each free atom in the hydrogen molecule has a magnetic moment of $\sqrt{3}\mu_B$, due to spin. However electrostatic interactions between the 2 atoms is such that the lowest energy state in the hydrogen molecule is filled with electrons of opposite spins and the magnetic moment is zero.



The hydrogen molecule is therefore diamagnetic and would be weakly repelled by a magnetic field due to Larmor precession.

A free oxygen atom has a magnetic moment of $3.67\mu_B$, due to two spin up electrons in the 2p subshell. In the oxygen molecule the lowest ten energy states of the hybrid 2p orbitals, are occupied such that the 2 electrons with the highest energy occupy separate orbitals with spinup.



Thus the oxygen molecule has a magnetic moment due to the 2 spin-up electrons. However the magnetic moments of molecules are randomly oriented so the bulk magnetisation is zero. The individual moments are capable of some alignment in an applied magnetic field. The oxygen molecule is therefore weakly attracted to a magnet at low temperatures, and is said to be paramagnetic.

6. Magnetism in metals (crystals).

In crystals the regular geometrical pattern of atoms interact with each other, such that the energy levels of the states in the various atoms are modified so that all the outermost states in the crystal have almost continuous energy levels. The inner electrons of the atoms remain associated with their particular nuclei but the outer electrons belong to the crystal as a whole. A crystal may be regarded as one very large molecule.

In metals the free electrons, which give rise to high electrical conductivity, can be considered to form a swarm of mobile valence electrons around a structure of fixed positive ions.

6.1 Ferromagnetic Iron

In the iron group the magnetic moments are due to electrons in the incomplete 3d sub-shell and there are strong electric fields between neighbouring ions. The interaction of these crystalline fields upon the orbital motions of the 3d electrons is very much greater than any applied magnetic field. Thus the multitude of orbital magnetic moments, which point in different directions and cancel each other out, cannot be aligned with a magnetic field and are said to be 'quenched'.

The ratio of total magnetic moment to angular momentum is given by the gyromagnetic ratio g .

$$\frac{\mu}{P} = g \frac{\mu_L}{P_L}$$

A g value of 2 would indicate that alignment of electron spins is responsible for magnetisation, while a value of 1 would indicate that it was due to changes in the orientation of orbital motions.

Gyromagnetic experiments involve changing the magnetism and measuring the resulting change of angular momentum to determine g . Experimental values of g are:

Iron ≈ 1.94 , Cobalt ≈ 1.87 , Nickel ≈ 1.92

These values all approach 2 and show that ferromagnetism is mainly due to the spin motion of

electrons, although the fact that g is less than 2 indicates a small contribution due to orbital motion.

Due to electrostatic coupling over the particular interatomic distances involved in ferromagnetic crystals the spin magnetic moments of adjacent atoms line up spontaneously to create small magnetic domains in the crystal which are magnetised to saturation.

Although these magnetised domains point in different directions and tend to cancel each other out, they can be very easily aligned by a magnetic field.

6.2 Diamagnetic Copper

In metallic copper the single spin-up electron in the 4s subshell results in conduction. There are as many conduction electrons as there are atoms, and it might be thought that these would contribute to magnetism since they all have a magnetic moment of $1\mu_B$ due to spin. However in metallic copper the interatomic interaction between neighbouring atoms cause the lower energy 4s states to be filled with electrons having different spins. Thus there is no resultant magnetic moment and copper is in fact diamagnetic.

7. CONCLUSION

The fundamental principles of magnetism have been briefly examined in this paper. It should give the reader a good conceptual understanding of the magnetisation process, and serve as an introduction to the field of ferromagnetics.

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