Magnetochemistry
Magnetochemistry- Part I

Introduction

Magnetochemistry is the study of magnetic properties of materials. Magnetism is a property of matter in which there is a force of repulsion or attraction between like or unlike poles. Only a few solid materials are naturally magnetic. Magnetism arises from moving charges, such as an electric current in a coil. However, magnetic interaction can also be present in a material where no current is present.

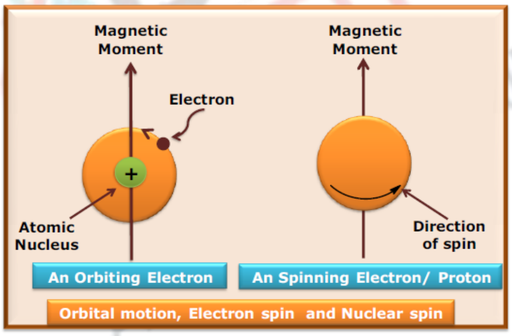


Fig. 1

Electrons in most atoms exist in pairs, with each electron spinning in an opposite direction. The spinning electron creates a magnetic field around it. In most of the materials the magnetic field of one electron is cancelled by opposite magnetic field produced by the other electron in the pair. The atoms in materials such as Fe, Co and Ni have unpaired electrons, their magnetic field is not cancelled by other electrons. As a result, each atom of these elements acts like a tiny magnet.

The processes which create magnetic fields in an atom are

(a) **Nuclear spin:** Some nucleus (such as H-atom) has a net spin which creates a magnetic field.

(b) **Electron spin:** An electron has two intrinsic spin states viz. up and down or α and β spin.

(c) **Electron orbital motion**: Magnetic field due to the electron moving around the nucleus.

Each of these magnetic fields interact with one another and with external magnetic fields. Some of such interactions are strong and some are weak (negligible).

Definitions of some magnetic properties

A dipole (or a bar magnet) consists of a positive (or north-seeking pole) and a negative (or a south seeking pole) pole separated by a small distance. At the pole, the magnetic effect is strong (Fig. 2).

A dipole generates its own magnetic field/flux (Fig. 3) and this can be mapped out from the directions assumed by a small compass needle suspended in the field. The North end of a compass will align itself with the field such that it points toward the south pole of the magnet

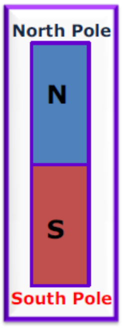


Fig. 2

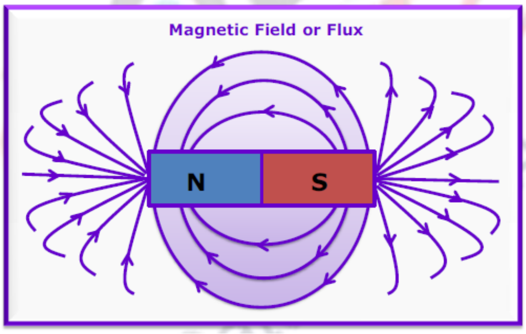


Fig. 3

(a) **Pole strength:** The strength of a magnet may be expressed in terms of a unit pole. It is defined as the strength at which it repels or attracts a similar pole placed at 1cm distance, with a force of 1 dyne. A unit intensity of magnetic field exists at the point where the unit pole experiences 1 dyne force (Fig. 4).

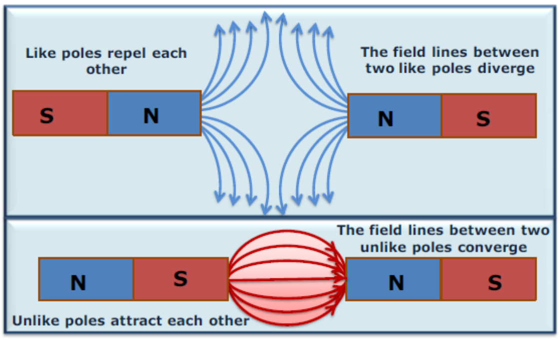


Fig. 4

Pole Strength is the measure of the force exerted by one face of a magnet on the face of another magnet, when both are represented by equal and opposite poles.

(b) Pole strength and lines of force: A magnetic field of unit intensity is taken to give a unit lines of force per cm^2. If a pole of strength m is enclosed in a sphere of radius 1 cm, a total of 4πm lines of force will eliminate from the pole (surface area of sphere 4πcm^2) (Gauss's law). The number of lines of force per cm^2 at the surface of sphere is given by,

$$\frac{\boldsymbol{4\pi m}}{\boldsymbol{4\pi \times 1\ cm^2}} = m \qquad (1)$$

(c) **Magnetization (M)**: When a magnetizable material is placed in a magnetic field it becomes magnetized in the direction of the applied field. The intensity of this induced magnetization is expressed in terms of the pole strength induced per unit area (A),

$$M = m/A$$

(d) **Intensity of magnetization (I):** The intensity of magnetization (I) induced in a body by an applied magnetic field is expressed in terms of the pole strength induced per unit area (A), i.e.,

$$I = \frac{\mathrm{m}}{\mathrm{A}} \qquad (2)$$

This is a situation for hypothetical monopole. For dipole (real) of length 'l' and pole area 'A' we have

$$I = \frac{\mathrm{m \times l}}{\mathrm{A \times l}} = \frac{\text{magnetic moment}}{\text{volume}} \qquad (3)$$

The intensity of magnetization may be alternatively defined as magnetic moment per unit volume.

(e) **Magnetic field or magnetic induction:** When a body is subjected to a magnetic field, the field produced within the sample will be either greater or less than the applied field, depending on whether the material is paramagnetic or diamagnetic. If H is the strength of the applied field, B is the induced field inside the sample (magnetic induction) and ΔH is the additional field generated due to induced magnetization,

$$\Delta H = B - H \qquad (4)$$

ΔH will be negative ($B < H$) for a diamagnetic and positive ($B > H$) for paramagnetic substances.

Alternatively, when a material is placed in a magnetic field, the magnetic field inside the material will be the sum of the external magnetic field and the magnetic field generated by the material itself.

$$B = H + \Delta H \qquad (5)$$

The difference between the applied field (H) and that induced in the sample can be expressed in terms of intensity of magnetization, I.

$$B = H + \Delta\mathrm{H} = H + 4\pi I \qquad (6)$$

Because both B and I will tend to be proportional to an external field, dividing it by H_o will give ratios (I/H_o and B/H_o) which are essentially constant for a given substance.

(f) **Magnetic permeability (P):** Magnetic permeability is the measure of ability of a material to support the creation of a magnetic field within itself. In other words, it is the degree of magnetization that a material attains in response to an applied magnetic field. The reciprocal of magnetic permeability is magnetic reluctivity

Magnetic Permeability (P) is the ratio of the density of the magnetic lines of force within a sample and that under vacuum. Mathematically, it is defined as

$$P = \frac{density\ of\ lines\ of\ force\ within\ body}{density\ of\ lines\ of\ force\ under\ vacuum} = \frac{B}{H} = 1+4\pi(\frac{I}{H}) = 1 + 4\pi\kappa \qquad (7)$$

κ is the volume magnetic susceptibility (magnetic susceptibility per unit volume)

In SI units, permeability is measured in Henries per meter (Hm^{-1}), or Newtons per ampere square (NA^{-2}).

The permeability constant (P_o), also known as the magnetic constant or the permeability of free space, is a measure of the amount of resistance encountered when forming a magnetic field in a vacuum. The magnetic constant has the exact (defined) value, that is,

$P_o = 4\pi\times10^{-7} \approx 1.266 \times 10^{-6}\ \mathrm{Hm}^{-1}$ or NA^{-2}

Relative magnetic permeability (P_r) is ratio of the permeability of a specific medium (P) to the permeability of free space, P_o

(g) **Volume Magnetic susceptibility (κ or χ_V):** It is a response of a substance to induced magnetization. Mathematically, the ratio I/H is the magnetic moment per unit volume per unit magnetic field and is defined as the volume magnetic susceptibility (κ) of the body. It is a characteristic property of a compound (I is proportional to H).

$$\kappa = \frac{I}{H} \qquad (8)$$

Value of κ is negative for a diamagnetic and positive for paramagnetic substances. It is a dimensionless quantity.

(h) **Specific (gram) susceptibility (χ_g) and molar susceptibility (χ_M):** The quantity that is most frequently obtained from experimental measurements of magnetism is the specific/mass/gram susceptibility (χ_g). It is related to the volume susceptibility through the density, i.e.,

$$\chi_g = \frac{\kappa}{\rho} = \frac{\chi_v}{\rho}, \qquad (9)$$

where ρ is the density of a substance and κ or χ_v is the volume susceptibility and χ_g is termed as specific (gram) susceptibility.

Multiplying the specific susceptibility of a compound by its molecular weight (M) gives the molar susceptibility, i.e., Molar susceptibility $(\chi_M) = \chi_g \times M$ (10)

Magnetic Moment

Instead of magnetic susceptibility, magnetic moment is more conveniently used in magnetochemistry. If a bar magnet is placed in a uniform magnetic field H, its poles + p and – p experience force pH and pH along and opposite to the direction of magnetic field H (Fig. 5); so net force on the bar magnet is zero. But the force being equal and opposite and having separation between their lines of action form a couple.

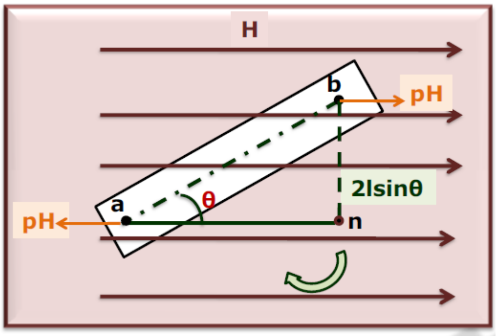


Fig. 5

The magnetic susceptibility of any substance is determined experimentally. The magnetic susceptibility is then converted to the magnetic moment using Curie equation. It should be noted that magnetic susceptibility is additive property, whereas it is the square of the magnetic moment that is additive.

Magnetic states of matter (classification according to magnetic properties)

(a) **Diamagnetism:** Diamagnetism is the characteristics ascribed to substances which are repelled by a magnetic field (attracted towards region where the magnetic field is weak). This is caused by the presence of closed shells of electrons/paired electrons (net spin zero). Since all compounds contain some paired electrons, diamagnetism is a universal property of matter (weak property). Ag, Cu, Au, Pb, Zn etc. contains only paired electrons and hence they are diamagnetic in nature.

In closed shell, the spin and orbital moments of the individual electrons balance each other, leaving no net magnetic moment. In presence of external magnetic field, there is an individual circulation of the electrons producing a net magnetic moment in opposition to the applied field. In fact, the induced magnetic moment does not influence the spins of the electrons which are paired, but the planes of the orbits are slightly altered. If a substance has only paired electrons, this effect will predominate, the material will be classified as diamagnetic.

Diamagnetism is independent of temperature. The magnetic permeability, P is less than 1 and κ is negative for a diamagnetic substance. Such substances allow a smaller number of lines of force to pass through it (compared to vacuum), and therefore prefers to move to the region of lowest magnetic field strength (Fig. 6).

The magnetization is in the opposite direction to that of the applied field, i.e. the magnetic susceptibility is negative. Diamagnetism is a very weak form of magnetism that is only exhibited in the presence of an external magnetic field. It is the result of changes in the orbital motion of electrons due to the external magnetic field. The induced magnetic moment (resulting from changes in the orbital motion of electrons due to the external magnetic field) is very small and, in a direction, opposite to that of the applied field (Fig. 7).

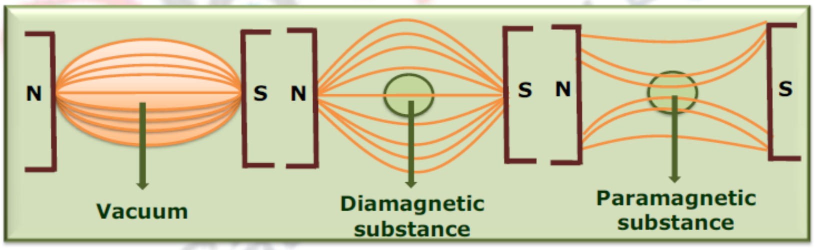


Fig. 6

(b) **Paramagnetism:** Paramagnetism is the property of substance which are attracted in a magnetic field with a force proportional to the product of field strength and field gradient. Paramagnetism derives from the spin and orbital angular moments of electrons. When all the electrons in a molecule are paired, their spin and orbital angular moments cancel each other. Hence, paramagnetism occurs only in substances with unpaired electrons; e.g. free atoms, free radicals, and compounds of transition metals containing ions with unfilled electron shells. It also occurs in metals because of the magnetic moments associated with the spins of the conducting electrons. Al, Cr, Mo, Na, Ti, Zr etc. possess unpaired electron in their valence shell and hence they behave as paramagnetic substance.

An electron has two different types of motions associated with it viz. orbital and spin motion. Since the electron is itself charged, the orbital motion is equivalent to the movement of a charge along a loop, which generates a magnetic field perpendicular to the plane of the orbit. Besides, the spinning of the electron about its own axis also is equivalent to the movement of a charge and thereby generates a magnetic field. The resulted molecular magnetic moments (permanent) tend to align themselves with an applied field. Thus, paramagnetism is a consequence of the interaction of orbital and/or spin angular momenta of unpaired electrons with the applied field.

Paramagnetic effect is much larger than diamagnetic effect, and the paramagnetic effect cancels any repulsion between an applied field and paired electrons in a sample. Thus, substances with only one unpaired electron will show a net attraction into a magnetic field. In a molecule, all atoms have a diamagnetic susceptibility, thus a measured molar susceptibility contained both paramagnetic and diamagnetic terms.

The paramagnetic effect is observed only in presence of external field. When the field is removed individual molecular moments are randomized by thermal motion and the bulk sample has no overall moment. In presence of the field, there is a competition between the thermal tendency towards randomness and the field's capacity to force alignment. Consequently, paramagnetic effects decrease in magnitude with rise in temperature.

The magnetic permeability, P is more than 1 and κ is positive ($B > H$) for a paramagnetic substance. Such substances allow many lines of force to pass through it (Fig. 6, as compared to that in vacuum), and therefore prefers to move to the region of highest magnetic field strength. In paramagnetism, the atoms or molecules of the substance have net orbital or spin magnetic moments that are capable of being aligned in the direction of applied field. This alignment of the atomic dipoles with the magnetic field tends to strengthen it (Fig. 7), and is described by a relative magnetic permeability greater than unity

Magnetically dilute and magnetically concentrated substances:

When the individual paramagnetic centers in a substance are efficiently apart so that there is no further interaction between neighboring centers, the substance is said to be magnetically dilute. $[Ni(H_2O)_5]Cl_2$ is an example of a magnetically dilute substance. In such substance, the paramagnetic centers are separated from one another by several diamagnetic species, e.g., the water molecules in the hydrate Ni ions. Majority of coordination complexes are magnetically dilute; the paramagnetic centers are usually linked to ligands where the donor atoms are considerably separated from each other by other atoms. As a result, no secondary magnetic interaction is possible between the neighboring paramagnetic centers.

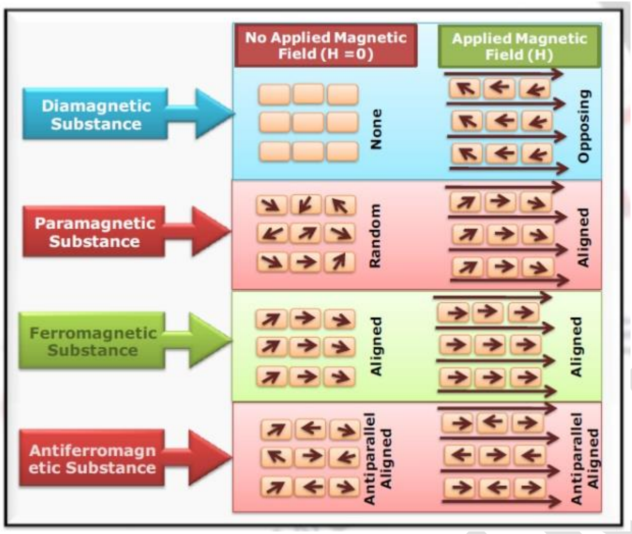
However, in a magnetically concentrated substance the individual magnetic centers are sufficiently close to allow further magnetic interaction. There are some paramagnetic substances in which secondary interaction exists between the neighboring magnetic centers. Such a substance is known as magnetically concentrated. Such interaction may lead to a decrease or increase in the magnetic moment (magnetic behavior) which is known as antiferromagnetism and ferromagnetism respectively. In $Cu_2(CN_3COO)_4.2H_2O$, the unpaired electron on the two Cu-atoms interacts with each other. In metals, the paramagnetic centers are close together and interact sufficiently with one another. Interaction may also occur when the paramagnetic centers are separated only by an atom or a monoatomic ion that may transit magnetic interaction. The interaction in it may lead to (1) an increase or (2) a decrease in the magnetic moment. A substance of the type (1) is called Ferromagnetic, and type (2) is called Antiferromagnetic. Of the magnetically concentrated coordination complexes, most are antiferromagnetic and very few are ferromagnetic. Antiferromagnetism may arise via (i) metal-metal interaction, as in $Mn_2(CO)_{10}$ and (ii) superexchange through one or more bridging atoms (O, N. F, Cl and S), as in many Cu (II), oxovanadium (IV) and oxomolybdenum (V) complexes of tridentate dibasic ONO donor Schiff's bases like N-(hydroxyphenyl)salicylideneimine.

(c) **Ferromagnetism:** It is a phenomenon observed in magnetically ordered materials in where there is a bulk magnetic moment and the magnetization is large. The electron spins of the atoms in microscopic regions, domains, are aligned. In the presence of an external magnetic field the domains orient favourably with respect to the field grow at the expense of the others and magnetization of the domains tends to align with the field (Fig. 7).

Ferromagnetism is observed when the magnetic vectors of adjacent centers align parallel to each other (energetically favorable). The total magnetic moment of a substance is the vector sum of the magnetic moments of component domains. Ferromagnetism is a phenomenon by which a material can exhibit a spontaneous magnetization, and is one of the strongest forms of magnetism. Ferromagnetism is greatly enhanced paramagnetism due to close alignment of magnetic dipoles in the same direction. It is responsible for most of the magnetic behavior encountered in everyday life, and is the basis for all permanent magnets (as well as the metals that are noticeably attracted to them).

In a ferromagnetic substance, there are unpaired electron spins, which are held in alignment by a process called ferromagnetic coupling. At high temperatures, the susceptibility obeys a Curie-Weiss law with negative θ. As the temperature is lowered, the susceptibility increases more rapidly than expected, the prelude to an abrupt, very large, increase in susceptibility. Above Curie temperature (T_c), thermal agitation overcomes the aligning tendency and as a result the ferromagnetic substance behaves as normal paramagnetic one. Ferromagnetic substances have their magnetic permeability very much greater than unity. Surprisingly few compounds prove to be ferromagnetic: a small number of metals and alloys, a fair range of oxides (CrO_2), and few transition metal halides.

(d) **Antiferromagnetism:** Antiferromagnetism (opposite of ferromagnetism) arises when the magnetic moments at neighboring centers are aligned in opposite (antiparallel) directions (Fig. 7). As a result of anti-parallel alignment of spins in two interpenetrating structures, there is no overall bulk spontaneous magnetization. Antiferromagnetic materials have a negative coupling between adjacent moments and low frustration. Increasing the temperature will tend to randomize the alignment and the susceptibility rises to a maximum at the Neel Point (T_N). Above T_N, the susceptibility falls, ultimately obeying Curie-Weiss law, usually with positive θ. The susceptibility is usually only weakly field-dependent below T_N. Such a substance is strongly repelled by a magnet. Antiferromagnetic materials are relatively uncommon. MnO is antiferromagnetic (antiparallel alignment) below 118°C. Another example is the heavy-fermions superconductor URu_2Si_2.



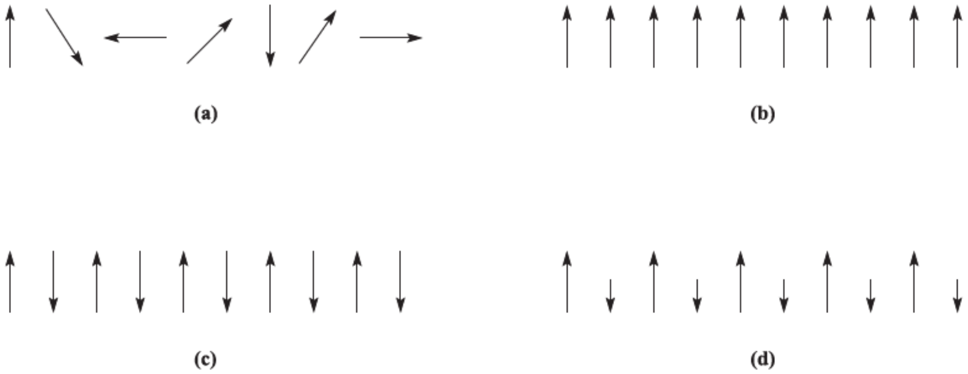


Fig. **7:** Schematic representation of magnetic dipole arrangement in (a) paramagnetism, (b) ferromagnetism, (c) antiferromagnetism and (d) ferrimagnetism materials.

(e) **Ferrimagnetism:** Ferrimagnetism is shown by substances in which the individual magnetic moments are symmetrically aligned to oppose others but giving rise to some finite resultant magnetic moment. The arrangement of electrons is known as ferromagnetic coupling. In ferrimagnetism, there is ferromagnetic ordering in a layer, coupled with antiferromagnetic ordering between layers. The antiferromagnetic ordering does not lead to a cancellation of moments on the two sub-lattices. Such an arrangement is said to be ferrimagnetic (attracted by magnet). Fe_3O_4 is ferrimagnetic in which magnetic moments of octahedral sites are aligned in one direction and that of tetrahedral sites in opposite direction.

Theory of Diamagnetism

Diamagnetism is the phenomenon of inducing magnetic field in a material which opposes it. A diamagnetic material has a negative magnetic susceptibility. The diamagnetic susceptibilities are very small in magnitude compared to paramagnetic materials and negligible compared to ferromagnetic materials. The universally accepted explanation of diamagnetism is the precession of the magnetic moment created by the orbital motion of electrons. Diamagnetism can be explained by (1) Classical theory of diamagnetism, and (2) Quantum-mechanical theory of diamagnetism.

Quantum-Mechanical Theory of Diamagnetism: The quantum-mechanical theory of magnetic susceptibilities has been treated by Van Vleck. The expression for diamagnetic susceptibilities using Quantum mechanical theory is the same as that by classical theory. The atomic diamagnetic susceptibility of hydrogen may be calculated directly from the expression

$$\chi_A = -2.832 \times 10^{10}\left\{\frac{h^2}{4\pi^2 Ze^2 m}\right\}\left[\frac{5}{2}n^4 - \frac{3}{2}n^2 l(l+1) + \frac{1}{2}n^2\right]$$

$$= -0.790 \times 10^{-6}\left\{\frac{5n^4 - 3n^2 l(l+1) + n^2}{2Z^2}\right\}$$

where n and l are the principal and azimuthal quantum numbers respectively and Z is the atomic number. The quantity h is Planck's constant and m is the mass of an electron. For atomic hydrogen n = 1, l = 0, and Z = 1, hence the gram-atomic susceptibility is - 2.37 × 10^{-6}. Almost similar types of calculations can also be performed for helium and heavier atoms.

Some important points about diamagnetic susceptibility are

1. It is negative, i.e., it opposes the applied magnetic field.
2. It is an inherent property of a substance containing paired or unpaired electrons. However, it can be usually detected in a compound containing paired electrons. The unpaired electrons being paramagnetic overshadow diamagnetism.
3. Diamagnetism depends only on the radius (r) of electronic orbits.
4. It is independent of temperature. A slight variation in the diamagnetic susceptibility with a change in temperature must be viewed in the light of expansion or contraction in the electron orbit.
5. Diamagnetism is an induced effect and exists as long as H lasts.

Sources of Paramagnetism

An electron has two motions associated with it.

1. It is going around the nucleus in an orbit. Since the electron itself is charged, this orbital motion is equivalent to the movement of a charge along a loop, which generates a magnetic field perpendicular to the plane of the orbit (Fig 8). Thus, the moment resulting from electron 'orbiting' the nucleus is the orbital magnetic moment denoted μ_L
2. Other motion is the spinning of electron about its own axis, which too is equivalent to the movement of a charge and generates a magnetic field (Fig. 8). The magnetic moment resulting from electron spin is denoted μ_S and is called the spin magnetic moment.

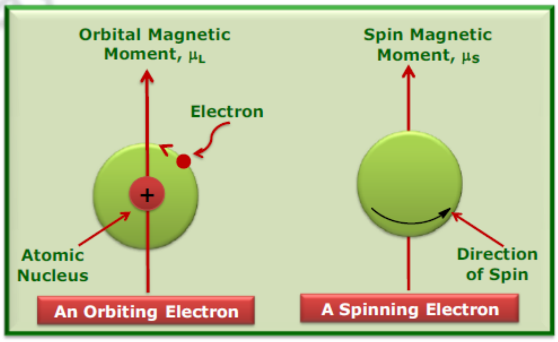


Fig. 8

Orbital Magnetic Moment

Let us assume that a single electron of charge e and mass m is moving about a nucleus O with an average angular velocity ω (Fig. 9). The number of revolutions per second the electron makes is then ω/2π. The current it carries per second is eω/2πc emu (c is the velocity of light). According to the principles of electrodynamics, such an orbiting charge generates a magnetic field whose moment is given by

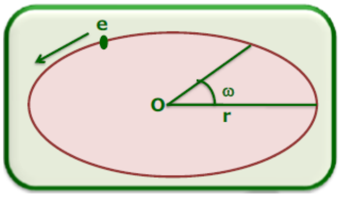


Fig. 9

Orbital magnetic moment, μ = strength of current (I) x area of the orbit (A)

$$= (e\omega/2\pi c) \times \pi r^2 = e w r^2/2c$$

r is the mean square radius of the orbit.

Such a relation has little utility if it cannot be expressed in the form that includes the quantum number characteristic of the electron movement. An electron has characteristic angular momentum which is expressed as orbital angular momentum quantum number (l). As we know,

$$\text{Orbital angular momentum} = m\omega\overline{r^2} = \sqrt{l(l+1)}\frac{h}{2\pi}$$

where h is plank's constant. So, the orbital angular moment μ_l is given by

$$\mu_l = \frac{e\omega r^2}{2c} = \sqrt{l(l+1)}\frac{eh}{4\pi mc} = \sqrt{l(l+1)}\,\beta$$

where β is the Bohr magneton, unit of magnetic moment, and its magnitude is given by

$$\beta = \frac{eh}{4\pi mc} = 0.917 \times 10^{-20}\,\text{erg oersted}^{-1}$$

Spin Magnetic Moment

As we can see, the ratio of orbital magnetic moment ($e\omega r^2/2c$) and orbital angular momentum $m\omega r^2$ is $e/2mc$. For spinning electron, the ratio of spin magnetic moment and spin angular momentum is $e/(mc)$. Therefore, we can write,

Spin magnetic moment (μ_s) = spin angular momentum × $e/(mc)$

$$\mu_s = \sqrt{s(s+1)}\,[h/2\pi] \times [e/(mc)]$$

$$\mu_s = 2\sqrt{s(s+1)}\frac{eh}{4\pi mc} = 2\sqrt{s(s+1)}\,\beta$$

$$\mu_s = \sqrt{4s(s+1)}\,\beta$$

where s stands for the spin quantum number. This is called spin-only formula. For any system, S = n (1/2) = n/2; n = no of unpaired electrons. Hence

$$\mu_s = \sqrt{4 \times \frac{n}{2}\left(\frac{n}{2}+1\right)}\,\beta$$

$$\mu_s = \sqrt{n \times (n+2)}\,\beta$$

Orbital angular moment (μ_l) and spin magnetic moment (μ_s) are often written as

$$\mu_l = g\sqrt{l(l+1)}\,\beta \quad (g = 1)$$

$$\mu_s = g\sqrt{s(s+1)}\,\beta \quad (g = 2)$$

where g represents the gyromagnetic ratio (the ratio of spin magnetic moment (μ_s) to the spin angular momentum$\sqrt{(s(s+1))}$). The magnetic moment of an atom is obtained from the sum of orbital magnetic moments and spin magnetic moments from all of the electrons in the atom. Some atoms will have a total magnetic moment and others will not.

For multi-electron systems,

$L = l_1 + l_2 + l_3 \ldots\ldots\ldots$

$S = s_1 + s_2 + s_3 \ldots\ldots\ldots$

Total magnetic moment of an atom,

$$\mu_{l+s} = \sqrt{4S(S+1) + L(L+1)}\,\beta$$

Magnetic Moment (Spin and orbital contribution)

The paramagnetic magnetic moment originates from the spins and orbital motions of the unpaired electrons in the substance. There are three possible modes of coupling between these components: spin-spin, orbital-orbital and spin-orbital. The magnetic moment of a free atom or ion may be calculated by using the resultant of spin (S) and angular momentum quantum (L) numbers and total angular momentum quantum (J, J = S + L).

For some complexes, particularly those of the lanthanides and actinides, all the three types of coupling are considered. The theoretical magnetic moment for such a complex is given by

$$\left.\begin{aligned} &\mu_{\text{eff}} = g_J\sqrt{J(J+1)} \\ \text{where} \quad &g_J = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \end{aligned}\right\}$$

g_J is the Lande splitting factor for the electron and the value of J depends on the orbital angular momentum quantum number (L) and the total spin quantum number (S).

For metal ions of 3d series, spin-orbit coupling is non-existent or negligible but spin and orbital contributions are both significant. The spin and orbital angular momenta of the electrons interact independently with an external magnetic field and the predicted expression for μ is given by

$$\mu_{\text{eff}} = \sqrt{4S(S+1) + L(L+1)}$$

Actual orbital contribution is always somewhat less than the ideal value (above equation never fully realized in complexes). This is because; the orbital angular momentum is reduced from what would be in the free metal ion by the presence of ligands. In the extreme case, where L is effectively zero, the orbital contribution to the magnetic moment is said to be quenched (complexes having A or E ground state, in octahedral d^3, d^4 (HS), d^5 (HS), d^6 (LS), d^7 (LS) and d^8 complexes). *(**Use this concept to explain the magnetic properties of 4d and 5d elements and their compounds).*

Furthermore, when a complex involves a first-row transition element (except a few), orbital contribution is generally ignored (even if the ground state is T). For the L=0 condition,

$$\mu_{\text{eff}} = \sqrt{4S(S+1)} = 2\sqrt{S(S+1)}$$

This is known as spin-only formula for magnetic moment. Again, S is related to the unpaired electrons (n) by S=n/2, the expression may be further simplified to

$$\mu_S = \sqrt{n(n+2)} \qquad \text{or} \qquad \mu_S = \sqrt{4s(s+1)}$$

Spin-only formula gives results that are in reasonably good agreement with the experimental results. The advantage of using these equations is that it gives magnetic moments which are independent of temperature and the magnitude of the external field. However, μ_{exp} for Co (II) and Ni (II) are higher than those expected from μ_S.

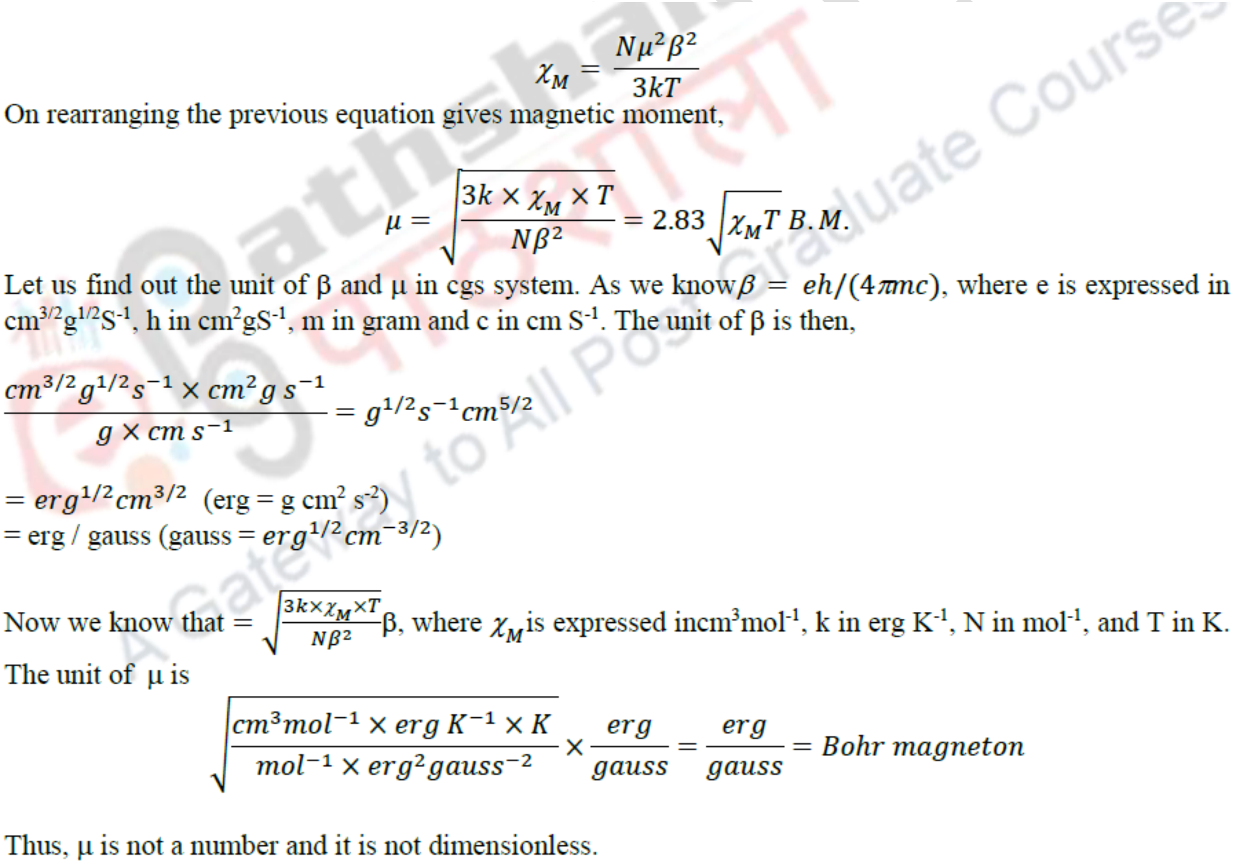
Paramagnetism and Temperature

The classical theory of paramagnetism was developed by Langevin on the assumptions that each atom is a little permanent magnet, and these atomic magnets tend to line up parallel to an applied magnetic field, but the alignment is resisted by the thermal agitation of the atoms. There is an obvious identification of the hypothetical atomic magnets with the magnetic moments induced by orbital electronic motion. Langevin deduced the following expression for the molar paramagnetism;

$$\chi_M = \frac{N\mu^2}{3kT}$$

where N is Avogadro's number, μ is the permanent moment, k the Boltzmann constant, and T is the absolute temperature. A precise expression will also include a term for relatively small diamagnetic part of the susceptibility. The above expression is applicable only to cases where molecular interactions are negligible. In case of paramagnetism, χ_M is inversely proportional to the absolute temperature, however, in case of diamagnetism, χ_M is independent of the absolute temperature (Fig 8). This theoretical prediction is fulfilled experimentally for a very large number of substances

μ is expressed in emu in previous equation. But more popularly, μ is expressed in Bohr magneton (B. M.), so the equation becomes



$$\chi_M = \frac{N\mu^2\beta^2}{3kT}$$

On rearranging the previous equation gives magnetic moment,

$$\mu = \sqrt{\frac{3k \times \chi_M \times T}{N\beta^2}} = 2.83\sqrt{\chi_M T}\ B.M.$$

Let us find out the unit of β and μ in cgs system. As we know $\beta = eh/(4\pi mc)$, where e is expressed in $cm^{3/2}g^{1/2}S^{-1}$, h in cm^2gS^{-1}, m in gram and c in cm S^{-1}. The unit of β is then,

$$\frac{cm^{3/2}g^{1/2}s^{-1} \times cm^2 g\, s^{-1}}{g \times cm\, s^{-1}} = g^{1/2}s^{-1}cm^{5/2}$$

$= erg^{1/2}cm^{3/2}$ (erg = g cm^2 s^{-2})
= erg / gauss (gauss = $erg^{1/2}cm^{-3/2}$)

Now we know that = $\sqrt{\frac{3k \times \chi_M \times T}{N\beta^2}}\beta$, where χ_M is expressed in cm^3mol^{-1}, k in erg K^{-1}, N in mol^{-1}, and T in K.

The unit of μ is

$$\sqrt{\frac{cm^3mol^{-1} \times erg\,K^{-1} \times K}{mol^{-1} \times erg^2 gauss^{-2}}} \times \frac{erg}{gauss} = \frac{erg}{gauss} = Bohr\ magneton$$

Thus, μ is not a number and it is not dimensionless.

Alternatively,

Magnetic moment (μ) of a substance cannot be determined experimentally. For determination of μ, first magnetic susceptibility (χ) of the substance is determined and the same is then used for determining μ. The corrected of paramagnetic magnetic molar susceptibility (χ_M) is related to the permanent paramagnetic moment (μ) of a molecule by

$$\chi_M = (N_A^2\mu^2)/(3RT) \qquad (11)$$

where N_A is Avogadro's number, R is the universal gas constant, T is the absolute temperature and μ is expressed in Bohr magnetons (BM) (1BM=eh/4πm = 9.274×10^{-24} JT^{-1}). Solving this expression for the magnetic moment gives

$$\mu = (3RT\chi_M/N_A^2)^{1/2} = 2.84\,(\chi_M T)^{1/2} \qquad (12)$$

Temperature dependence of magnetic susceptibility (Variation with Temperature):

The source of variation of magnetic properties with temperature is the disruption of the alignment of individual magnetic moments (dipoles) due to the thermal motion (agitation) of the atoms. The temperature dependence of magnetic susceptibility of diamagnetic, paramagnetic, ferromagnetic, and antiferromagnetic materials is shown (Fig. 10) below:

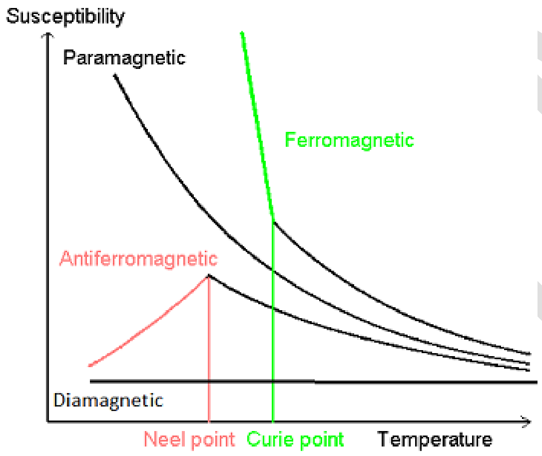


Fig. 10: Variation of magnetic susceptibility with temperature (transition to paramagnetic behavior of ferromagnetic and antiferromagnetic subatances ocuur at Curie and Neel teperature respectively)

A diamagnetic substance has its magnetic susceptibility invariant to temperature whereas the magnetic susceptibility of a paramagnet follows an inverse relation with temperature (decreases with rise in temperature). A ferromagnetic substance has a characteristic temperature (T_c) above which it behaves like a paramagnet, but below this temperature, its magnetic susceptibility increases rapidly. In ferromagnetic material, a transition takes place at lower temperature when all the individual magnetic moment aligns. Above T_C, thermal agitation is sufficient to overcome the tendency for alignment and thus normal paramagnetic behavior is observed. Below T_C, the tendency for alignment dominates and molar susceptibility is higher than expected. However, an antiferromagnetic possesses a characteristic temperature (T_N) above which it behaves like paramagnet, but below this temperature, its magnetic susceptibility decreases with decreasing temperature. In this case, the individual magnetic dipoles tend to align themselves to cancel out each other. Below T_N, such alignment causes lowering of susceptibility while above T_N, thermal agitation becomes sufficient to randomize such orientations and the substances show paramagnetism.

Temperature dependence of paramagnetism

Curie's law:

P. Curie (1895) studied the paramagnetism susceptibility of various substances at different temperature and established that paramagnetic susceptibility is inversely proportional to the absolute temperature.

$$\chi_M = \frac{C}{T} \qquad (13)$$

where 'T' is the absolute temperature and 'C' is a constant termed as Curie constant and is characteristic of a paramagnetic substance. The above relation is known as Curie law and is obeyed well by paramagnetic substances that are magnetically dilute. The constant C is given by the Langevin expression $C = N\mu^2/3k$

It may be noted that if magnetic susceptibility obeys the Curie's Law, then the magnetic moment is independent of temperature. Thus, a plot of $1/\chi$ versus T should give a straight line of slope 1/C passing through the origin (0K) (Fig. 11). This expression is approximately true for many solids, liquids, as well as for at least one of the two common paramagnetic gases, oxygen and nitric oxide.

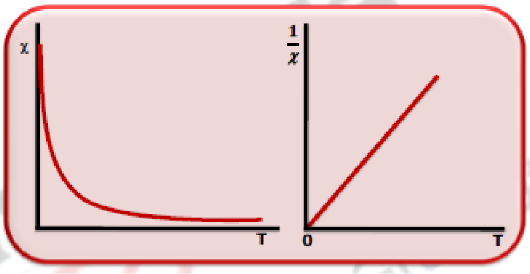


Fig. 11

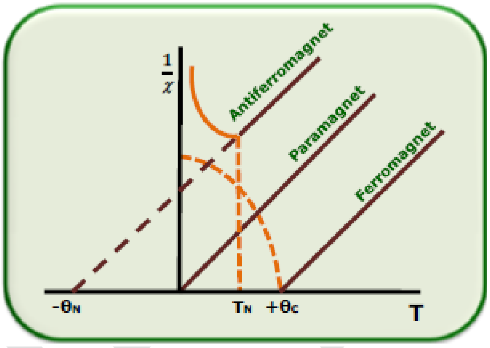


Fig. 12

Curie's Law is exhibited only

A) When the magnetic susceptibility arises entirely from the ground state and there are no thermally accessible states.

B) When the magnetic dipoles are completely independent of one another.

Among the ideal Curie paramagnets are $(NH_4)_2Mn(SO_4)_2.6H_2O$, $KCr(SO_4)_2.12H_2O$ and $Gd_2(SO_4)_3.8H_2O$.

Unfortunately, it has been observed that more accurate magnetic measurements lead to greater deviations from Curie's law are discovered. For many systems, a plot of $1/\chi$ versus T gives straight line, but the intercept is non-zero on the temperature axis (Fig 12). These systems do not follow Curie's Law due to following reasons:

a) There is some cooperative interaction between the neighbouring dipoles or

b) There are energy levels whose population changes with variation in the temperature or

c) The applied magnetic field induces some temperature-independent paramagnetism

Curie-Weiss law

There are many paramagnetic substances whose straight line does not pass through origin, leaves a finite intercept on the temperature axis. These materials are not magnetically dilute (ferromagnetic/antiferromagnetic). The unpaired spins on neighboring atoms may couple with each other, known as magnetic exchange. In any material that exhibits magnetic exchange, the tendency towards spin alignment will compete with thermal tendency favoring spin randomness. In all cases, there will be some temperature below which magnetic exchange dominates. This temperature is called the Curie temperature (T_C) if the exchange displayed is ferromagnetic and the Neel temperature (T_N) if it is antiferromagnetic (Fig. 11).

For such systems, Weiss obtained the following expression theoretically by considering mutual interaction (materials that display exchange behavior) of the elementary magnets or molecular magnetic fields

$$\chi_M = \frac{C}{T-\theta} \tag{14}$$

It is termed as Curie-Weiss law, where ‘θ’ is the intercept on the temperature axis and is known as Weiss constant (also referred to as the “molecular field constant with unit of temperature). The Weiss constant take care of the cooperative interaction. θ corrects the temperature for non-zero intercept, describes the so-called Curie-Weiss behavior. It is common to have non-zero intercept in the systems that are not magnetically dilute i.e., pure solid paramagnetic materials. In these systems, interionic or intermolecular interactions cause neighboring magnetic moments to become aligned and contribute to the value of intercept.

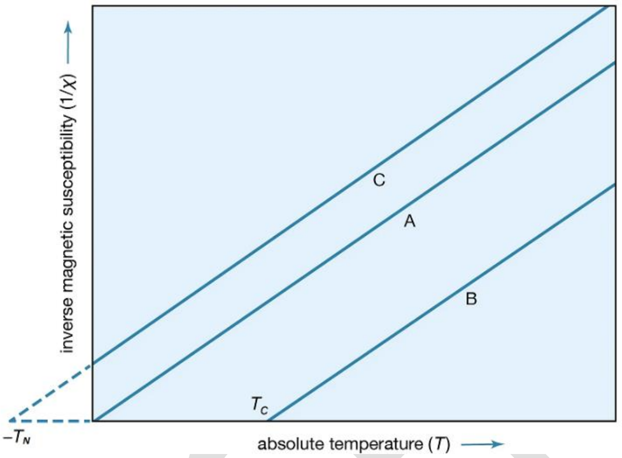


Fig. 11: Plots of reciprocal of magnetic susceptibility vs temperature of the three magnetic behaviors (a) Curie law (b) Curie-Weiss law for ferromagnetic substance with T_C and (c) Curie-Weiss law for antiferromagnetic substances with T_N.

For ferromagnetic substances, θ is positive (Fig. 12), whereas for antiferromagnetic substances, θ is negative (Fig. 13). The magnitude and sign of θ can be obtained from a plot of 1/χ versus T (Fig. 12). θ is replaced by the term Tc, Curie temperature for ferromagnetic substances. When ferromagnetic substances are heated beyond Curie temperature, they become paramagnetic (Fig 12). Curie temperature for Fe, Co, Ni and Gd are 770ºC, 1121ºC, 358ºC and 44ºC, respectively.

For antiferromagnetic substances (Fig. 13), θ becomes T_N, Neel temperature. χ reaches a maximum value at Neel temperature and then decreases with further fall in temperature. Therefore, a plot of 1/χ versus T should show a minimum at T_N. So, the antiferromagnetic substances when heated beyond Neel temperature, become paramagnetic (Fig. 13).

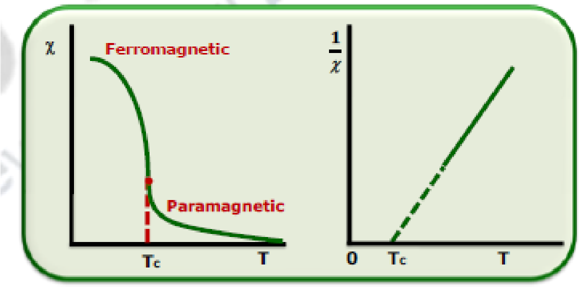


Fig. 12

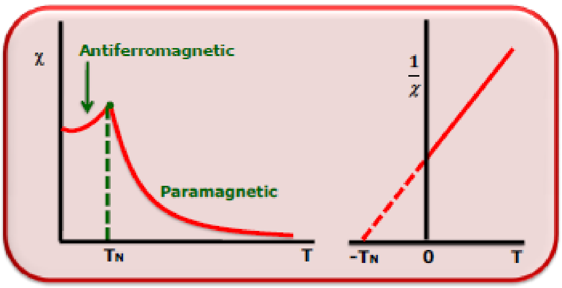


Fig. 13

In ferromagnetic substances, within a certain temperature range, there are net atomic magnetic moments, which line up in such a way that magnetization persists after removal of the applied field (Fig. 14). Above the Curie point, thermal motion is sufficient to offset the aligning force and the material becomes paramagnetic. Antiferromagnetic materials exhibit antiferromagnetism at a low temperature, and become disordered above a certain temperature; the transition temperature is called the Néel point. Above the Néel point, the material is typically paramagnetic (Fig. 14).

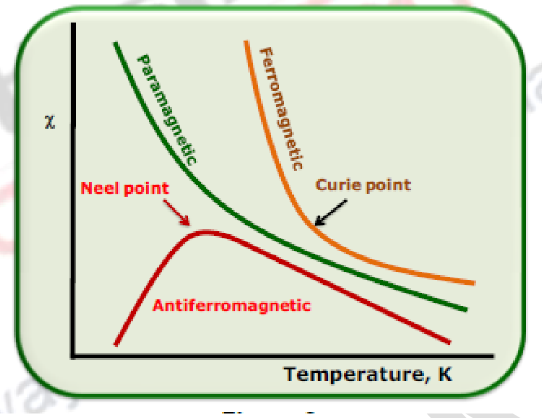


Fig. 14

Sometimes, θ have got negative value but the material does not show antiferromagnetic coupling. Therefore, a negative value of θ need not always implies an antiferromagnetic coupling. For example, titanium (III) caesium alum obeys the Curie-Weiss Law above 200K with θ = - 200K. When the temperature is lowered further, χ is levelled off to a constant value. This high negative value of θ cannot be assumed to mean a strong an antiferromagnetic coupling because

(a) The magnetic susceptibility vs. T curve does not reveal the usual maximum, i.e.T_N, the Neel temperature and

(b) The magnetic susceptibility determined experimentally does not fit the theoretical equation for antiferromagnetism.

When θ is taken from the 1/χ vs. T plot, the magnetic moment should be calculated using relation

$$\mu = 2.83\sqrt{\chi_M(T-\theta)}\ B.M.$$

Table 1: Comparison of four magnetic behaviors

Magnetic Property	Effect of external field	Specific susceptibility(χ) at 20°C, g^{-1}	Temp. dependence of χ	Field dependence of χ	Caused by
Diamagnetic	Weak repulsion	$-1x10^{-6}$	None	None	Paired, filled shell electrons.
Paramagnetic	Moderate attraction	$100x10^{-6}$	1/T	None	Unpaired electron spin and orbital motion.
Ferromagnetic	Very strong attraction	$1x10^{-2}$	Complex	Dependent	Neighboring particles with unpaired spins interacting among themselves.
Antiferromagnetic	Weakly attracted	$1x10^{-7}$-$1x10^{-5}$	Complex	Dependent	Neighboring particles with unpaired spins interacting among themselves.

Derivation of Curie Equation:

Curie equation relates the molar susceptibility and the magnetic moment of a substance. The multiplicity off M_J level is (2J+1).

In absence of external magnetic field, no splitting of the M_J level occurs. When a magnetic field (H) is applied, the J level splits. The projection, M_J, of J in the direction of H is quantized and can take values of J, J-1, ……..., -J. There are thus (2J+1) values of M_J each corresponding to a projection, ū, of μ.

$\mu = g\beta\sqrt{[J(J+1)]}$ and ū can therefore take the values $-g\beta J$, $-g\beta(J-1)$,………$+ g\beta J$, the signs of ū being reversed with respect to the corresponding M_J since, the magnetic moment is in exactly the opposite direction to the associated angular momentum vector.

The total spread of these levels is $2\mu H = 2g\beta JH$ and it follows that the separation between adjacent levels is $g\beta H$

The transitions between particular components, whether of the same multiplet or not, will vary slightly in energy depending on the change occasioned in M_J ($\Delta M_J = 0, \pm 1$). The normal Zeeman effect occurs for singlet lines and the anomalous Zeeman effect for non-singlets.

For material consisting of monatomic molecules ($\chi_A = \chi_M$) and ignoring the diamagnetic effects, intensity of magnetization I is defined as

$$I = \frac{\sum n\bar{\mu}}{V} \tag{1}$$

where *n* is here the number of atoms per gram mole with a particular projection of moment, ū, and *V* is the molar volume.

$$\chi = \frac{I}{H\rho} = \frac{I}{H}\frac{V}{M} \tag{2}$$

where *M* is the molecular weight.

$$\therefore \quad \chi_A = \frac{IV}{H} = \frac{\sum n\bar{\mu}}{H} \tag{3}$$

In order to determine the population of each level the Boltzmann distribution law is applied. The ratio of the number of molecules in the different levels is then seen to be

$$\exp\left(-\frac{g\beta JH}{kT}\right), \ldots \exp(0), \ldots \exp\left(\frac{g\beta JH}{kT}\right) \tag{4}$$

Since $g\beta H \ll kT$, *this* reduces to:

$$\left(1 - \frac{g\beta JH}{kT}\right), \ldots (1-0), \ldots \left(1 + \frac{g\beta JH}{kT}\right) \tag{5}$$

But for 1 g mole of material the total number of atoms is Avogadro's number *N* and, since there are 2J + 1 levels, the actual numbers of atoms in each level are

$$\frac{N}{(2J+1)}\left[1 - \frac{g\beta JH}{kT}\right], \ldots \frac{N}{(2J+1)}, \ldots \frac{N}{(2J+1)}\left[1 + \frac{g\beta JH}{kT}\right] \tag{6}$$

and ū for each level is

$$\frac{N}{(2J+1)}\left[-g\beta J + \frac{g^2\beta^2J^2H}{kT}\right], \ldots 0, \ldots \frac{N}{(2J+1)}\left[g\beta J + \frac{g^2\beta^2J^2H}{kT}\right] \tag{7}$$

On summation of these values the first term in each pair of brackets will cancel, leaving

$$\sum n\bar{\mu} = \frac{N}{(2J+1)} \cdot \frac{g^2\beta^2 H}{kT}[J^2+(J-1)^2 \ldots 0 \ldots (J-1)^2+J^2]$$

$$= \frac{2N}{(2J+1)} \cdot \frac{g^2\beta^2 H}{kT}[J^2+(J-1)^2 \ldots 0]$$

Now the sum, to the ith term, of a series of squares is

$$S_i = \frac{i(i+1)(2i+1)}{6}$$

$$\therefore \quad \sum n\bar{\mu} = \frac{2N}{(2J+1)} \cdot \frac{g^2\beta^2 H}{kT} \cdot \frac{J(J+1)(2J+1)}{6}$$

$$= \frac{Ng^2\beta^2 H}{3kT} \cdot J(J+1)$$

From equation (2)

$$\chi_A = \frac{Ng^2\beta^2}{3kT} J(J+1) \qquad (8)$$

Again, $\mu = g\beta\sqrt{[J(J+1)]}$ (9)

Combining equation (8) with equation (9)

$$\chi_A = \frac{N\mu^2}{3kT} \qquad (10)$$

where μ is measured in e.m.u.

$$\text{or} \qquad \chi_A = \frac{N\beta^2\mu^2}{3kT} \qquad (11)$$

where μ is measured in Bohr magnetons.

Putting the values of k, β (=eh/4πmc) we have

$$\mu = 2.83(\chi_A T)^{1/2} = 2.83(\chi_M T)^{1/2} \text{ B.M.} \qquad (12)$$

Equation (11) can also be expressed in the form

$\chi_M = C/T$ where, $C = N\mu^2\beta^2/(3k)$; is known as Curie constant and is a characteristic of paramagnetic substance.

Magnetochemistry- Part II

Temperature independent paramagnetism (TIP)

This is a kind of weak paramagnetic behavior independent of temperature which is shown by certain substances with or without any unpaired electron. Such behavior does not originate from any permanent magnetic dipole in the species in its normal state. The paramagnetism is induced when the substance is placed in a magnetic field which can effect a change in the ground state of the atom or ion. The higher energy excited states caused by the field can mix with the ground state and current can be stimulated by movement of the electrons to otherwise unoccupied higher energy orbitals. Such orbital paramagnetism gives rise to temperature independent paramagnetism (TIP). Since the substance has no permanent magnetic dipoles, the influence of thermal agitation on their alignment does not exist and hence the paramagnetism is temperature independent. Systems with low-lying excited states show such TIP (chromate and permanganate ions. both possess d^0 configuration).

Diamagnetic correction (χ_{dia}): The measured susceptibility for a given substance will consist of contributions from paramagnetic and diamagnetic susceptibilities, the former being much greater. The measured susceptibility is corrected by subtracting the diamagnetic contribution from it. Thus, Paramagnetic susceptibility = Measured susceptibility – Diamagnetic susceptibility

Ferromagnetism, Antiferromagnetism and Ferrimagnetism

The advantage of using effective magnetic moments for describing paramagnetic behavior is that it is a measure of the materials magnetic behavior which is not dependent upon either the temperature or the magnitude of the external field. It is not possible to set up such a convention for ferromagnetic, antiferromagnetic and ferrimagnetic materials.

All three of these classes of materials can be considered a special case of paramagnetic behavior. The description of paramagnetic behavior assumes that every molecule behaves independently. The materials discussed here result from a situation in which the direction of the magnetic field produced by one molecule is affected by the direction of the magnetic field produced by an adjacent molecule, in other words their behavior is coupled. If this occurs in a way in which the magnetic fields all tend to align in the same direction, a ferromagnetic material results and the phenomenon is called ferromagnetic coupling. Antiferromagnetic coupling gives an equal number of magnetic fields in opposite directions. Ferrimagnetic coupling gives magnetic fields in two opposite orientations with more in one direction than in the other.

With a few exceptions, the magnetic moments are not aligned throughout the entire material. The regions where magnetic moments are aligned are called domains, will form with different orientations. The existence of domains of coupled molecules gives rise to several types of behavior.

(a) The tendency of molecules to align themselves to one another enhances the magnetization of the material due to the presence of an external magnetic field. This is why ferromagnetic and ferrimagnetic materials can have magnetic susceptibilities several orders of magnitude large than paramagnetic materials. This also gives rise to the fact that the magnetic susceptibility of these materials is not independent of the magnitude of the external magnetic field as was the case for diamagnetic and paramagnetic materials.

(b) Vibrational motion of the molecules, which increases with temperature, can disrupt the domain structure. Thus, the magnetic properties of all three of these types of materials are strongest at low temperatures. At sufficiently high temperatures, no domain structure can form and all these materials become paramagnetic. The temperature at which paramagnetic behavior is seen called the

Curie temperature for ferromagnetic and ferrimagnetic materials and called the Neel temperature for antiferromagnetic materials. This is why a temperature independent effective magnetic moment cannot be defined for these materials.

(c) The alignment of the magnetic moments of the domains may give the material a net magnetic moment even in the absence of an external field. This gives a permanent magnet, such as a bar magnet. A material with no net moment prior to being exposed to an external magnetic field may retain a net moment after being exposed to an external magnetic field. This is how cassette and video tapes and computer disks store information. The magnitude of this memory effect can be quantified by plotting magnetization vs field strength as the external field intensity is varied from one polarity to the other and back again. A strong memory effect will be indicated by a wide hysteresis loop.

(d) Over a period, magnetic domains tend to return to a random orientation. This makes the kinetics of this relaxation process another factor in the magnetic behavior of these materials. This is also responsible for the limited life span of magnetically stored music, video, and computer data

Spin Cross-over: Spin state equilibrium (equilibrium between HS and LS state, HS-LS cross-over)

This phenomenon is commonly observed with some first-row transition metal complexes with a d^4 - d^7 electron configuration in octahedral ligand geometry. In certain cases, the same metal ion and ligand combination may give rise to both high spin and low spin complexes in the octahedral field. These spin state can coexist in equilibrium and greatly influenced by temperature. The metal ions with d^4, d^5, d^6, d^7 may give rise to high spin or low spin octahedral complexes depending on whether the magnitude of ligand field splitting parameter Δ_o or 10Dq is lower or greater than the mean pairing energy (P). Generally, for a LS complex $\Delta_o > P$ and for a HS complex $\Delta_o < P$. The HS and LS state of an octahedral complex with any of d^4, d^5, d^6 and d^7 configurations will have same energy when $\Delta_o = P$. If in a coordination complex, the crystal field splitting is close to critical $\Delta_o = P$ value, the energy difference between the two-spin state will be in the range of thermal energy kT. Further, in octahedral field, if the energy of the two spin states is same or nearly same, the low spin and high spin states can coexist in equilibrium. This phenomenon is referred to as spin-state equilibrium; the magnetic moment for these complexes will be anomalous. A change in the temperature will lead to an alteration in the population of the two spin states. If the ground state of the complex is LS, (a) an increase in the temperature will increase the population of the HS state i.e., magnetic susceptibility is increased, and (b) a decrease in temperature will increase the population of the LS state, i.e., the magnetic susceptibility is decreased. On the other hand, if the ground state is high spin, the reverse of (a) and (b) will hold.

An example of metal ion that can exist in HS or LS state in octahedral ligand field is Fe^{3+}. Fe^{3+} can attain a LS or a HS state and this is decided by the nature of ligands that are coordinated to the given complex, as in Fig. 1. Consider the low spin complex, $[Fe(CN)_6]^{4-}$(ground state ${}^1A_{1g}$) and the high spin complex, $[FeF_6]^{4-}$(ground state ${}^5T_{2g}$) of Fe^{2+} ion. The Tanube-Sugano diagram of $[Fe(CN)_6]^{4-}$ and $[FeF_6]^{4-}$ is shown in Fig. 2. Now, change in the temperature will lead to an alteration in the population of the two spin states. The Tanube- Sugano diagram of the two complexes reveals that if the ground state of the complex is low spin, then with increase in temperature the magnetic susceptibility will increase and with decrease in the same magnetic susceptibility will decrease. On the other hand, if the ground state is high spin, then the reverse of the above relationship between temperature magnetic susceptibility will be followed.

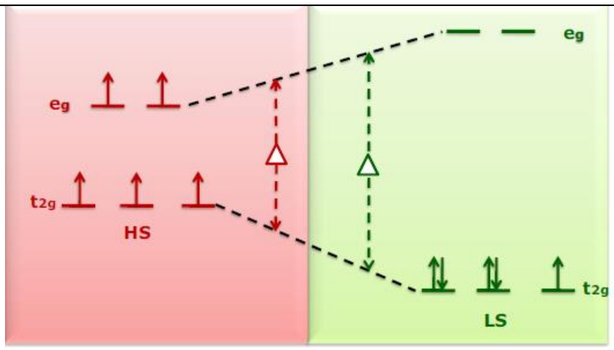


Fig. 1

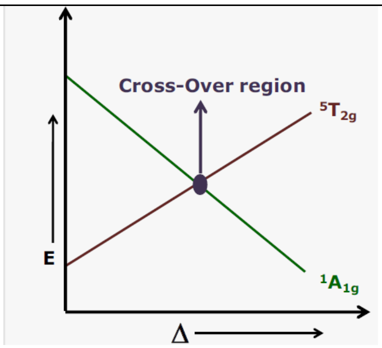


Fig. 2

In an octahedral complex, there exist a critical Δ_o and P values (in some cases), around which the HS and LS states will have about the same energy. This critical value is sometimes referred to as high spin-low spin crossover point. If we have a ligand whose field is close to this crossover point, its complex might be able to coexist in a measurable amount of both forms (HS and LS) at equilibrium. The slope of the two lines will depend upon the relative energies of the two states (compared to the free ion) as determined by Δ_0 and P. For d^5 metal ions the relative energies of high spin state will be zero and hence independent of Δ_o. The point A in Fig. 3 represents the high spin-low spin crossover point where Δ_o equal to P. On the left of A, the high spin state is more stable and on the right of A, low spin state will be more stable. In a limited range of Δ_o around the point A shown where $\Delta_o \approx P$ (values do not differ by more than 2000 cm^{-1}), the two spin states may exist in equilibrium with each other. This is then said to be spin isomers and the phenomenon is called spin isomerism.

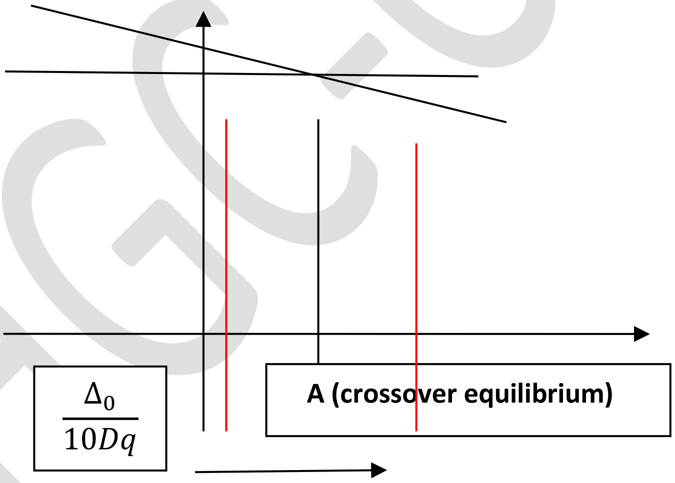


Fig. 3

The Tanabe- Sugano diagram of these d^6 complexes also show that near the crossover point between weak and strong field the difference in energy between the spin-free ($^5T_{2g}$) and spin-paired ($^1A_{1g}$) ground states becomes very small (Fig. 2). Within this region, it is reasonable to expect that both spin states may coexist in equilibrium and that the degree to which each is represented will depend on the temperature (Δ-P = kT). The most interesting example of spin crossover is $[Fe(phen)_2(NCS)_2]$ complex (Fig. 4). At high temperature this complex exists as high spin with four unpaired electrons and a moment consistent with four unpaired electrons is observed. But as the temperature is lowered, a sharp drop in magnetic moment is observed at 175K and the low spin form of the complex becomes dominant. This indicates that at 175K, $[Fe(phen)_2(NCS)_2]$ exist as both high spin and low spin complex. Thus, the magnetism of $Fe(phen)_2(NCS)_2$ changes sharply at 174K, as shown in Fig. 4.

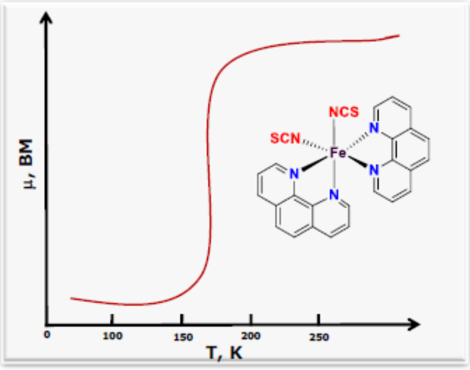


Fig. 4

In solution, these systems are straightforward; the change in magnetic susceptibility with temperature can be interpreted in the terms of heat of conversion of one isomer to another. However, treatment of the system as an equilibrium between two spins gives, ΔH=3.85 kcal mol-1 and ΔS = 11.4 for the high spin to low spin conversion. On the other hand, spin crossover in solids is a complex phenomenon because of cooperative structural changes and changes in the energy separation of high-spin and low-spin states with temperature.

The spin state equilibrium is not possible in an octahedral complex of a metal ion with d^8 configuration, Ni (II) complex. However, the spin state equilibrium is represented in several d^8 Ni (II) complexes which originates from a distortion of a regular geometry or arising from two distinct coexisting stereochemistry (thereby, leading to the two spin states S = 1, S=0). It is obvious that no spin state crossover region and hence no spin state equilibrium is possible in a complex with the tetrahedral geometry because such a complex can only be high spin $\Delta_t << P$.

Thermal spin transition occurs nearly exclusively with coordination complexes of 3d metal ions. Thermal spin transition is not expected for 4d and 5d transition metal compounds because strength of the ligand field increases notably (by ~ 50% from 3d to 4d and, also from 4d to 5d) relative to analogous 3d compounds and is generally much greater than the spin pairing energy; hence virtually all 4d and 5d transition metal complexes show LS behavior.

Spin Transition Curves

Spin crossover phenomenon can be represented by spin transition curves. In spin transition curves**,** T is plotted vs high-spin molar fraction, γHS. Fig. 5 shows a gradual spin transition (left), an abrupt transition with hysteresis (middle) and a two-step transition (right). (For a transition to be considered gradual, it typically takes place over a large temperature range, even up to several hundred K, whereas for a transition to be considered abrupt, it should take place within 10 K or less). γHS is calculated as follows

$$\gamma HS = [Fe]_{HS}/[Fe]_{total} = [Fe]_{HS}/([Fe]_{HS} + [Fe]_{LS})$$

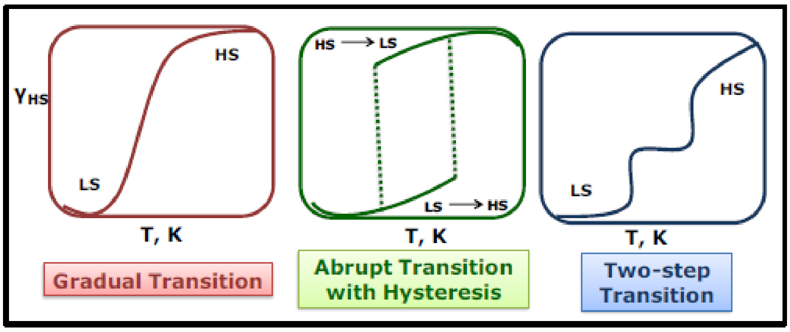


Fig. 5

These curves indicate that a spin transition has occurred in a metal complex as temperature changed. The gradual transition curve is an indication that not all metal centers within the complex are undergoing the transition at the same temperature. The abrupt spin change with indicates a strong cooperativity, or "communication", between neighboring metal complexes. In the latter case, the material can exist in the two different spin states with a different range of external stimuli (temperature in this case) for the two phenomena, namely LS→HS and HS→LS and is bistable. The two-step transition is relatively rare, but is observed, for example, with dinuclear SCO complexes for which the spin transition in one metal center renders the transition in the second metal center less favorable.

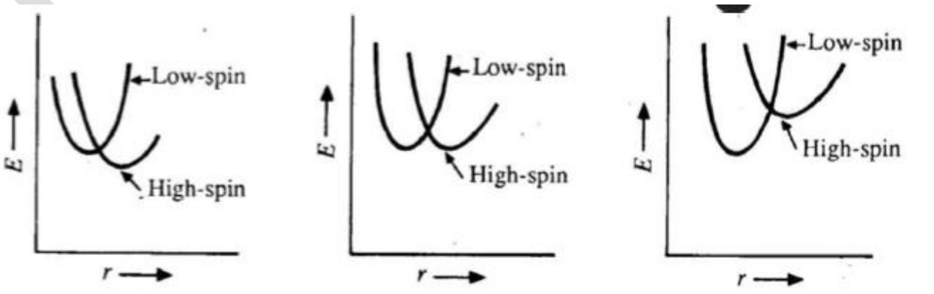
Factors affecting Spin Cross-Over (SCO) behavior

The cross-over region is very sensitive to several factors and both chemical and physical factors contribute significantly to it.

Chemical Factors

Effect of Metal-Ligand Bond Distance

The transition from high spin to a low spin state is carried out by the transfer of one (d^4 and d^7 configurations) or two (d^5 and d^6 configurations) electrons from the higher energy eg set (d_{x2-y2} and d_{z2} orbitals) to the lower energy t_{2g} set (d_{xy}, d_{xz} and d_{yz}). As we know that the eg set orbitals point directly at the ligands approaching right along the coordinate axis while the t_{2g} set orbitals are between the point charges. This enhances the repulsion between electrons of the metal e_g set orbitals and the donated electron pair from the ligand, raising the energy of these metal orbitals relative to the other three. Thus, an $e_g \rightarrow t_{2g}$ transition is most likely to reduce the metal-ligand bond distance (R). Since Δ is also dependent on R ($\Delta \alpha 1/R^5$), it follows that such a transition increases Δ by ~ 10-20 %. The potential energy curves for the high spin and low spin complexes are shown in Fig. 6. The low-spin state has its minimum energy at smaller R value than high spin state. Fig. 6, A and C depict high spin and low spin ground states, however, B shows the equilibrium situation, where energies of the two spin states are quite close, resulting in cross-over.



(a) High-spin (b) Cross-over situation (c) Low-spin

Potential energy curves for high-spin complexes, cross-over, and low-spin complexes.

Fig. 6

Effect of Intraligand Substitution

A substitution in the ligand backbone often changes Δ and B (interelectronic repulsion parameter) substantially due to

(1) The σ and π interactions

(2) The steric effects. This leads to a modification in the magnetic property. This has been illustrated with the group of $[Fe(Y\text{-}phen)_3]X_2$ complexes (Fig. 7) where Phen is 1,10-phenanthroline. Exchange of H for CH_3 in either the 2- or 9-position of the three phenanthroline ligands weakens the ligand field strength due to steric hindrance (whereby the metal–donor-atom distance is elongated) and the low spin behavior of $[Fe(phen)_3]X_2$ turns to SCO behavior of the tris(2-CH_3-phen) complex. If both the 2- and 9-positions of these three phen ligands are substituted by CH_3 the steric hindrance is even stronger and weakens the ligand field strength further, yielding high spin behavior of the tris[2,9-$(CH_3)_2$] complex down to very low temperatures. It was found that a combination of steric hindrance due to bulkiness and an electronic influence of the substituent on basicity of the coordinating N-atom are responsible for the influence on the SCO behavior. The paramagnetic property of the complex (given by the molar fraction of HS molecules, γHS, at a given temperature), increases in the order Y = H < CH_3O < CH_3 < Cl. One has also found that a change of the substituents at positions not adjacent to the coordinating N-atom in the phen ligand does not influence the spin state in comparison to the unsubstituted $[Fe(phen)_3]X_2$ complex.

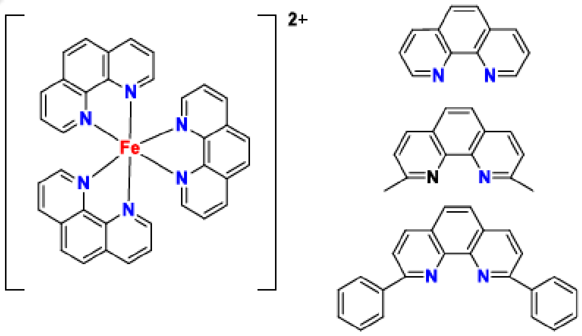


Fig. 7

Effect of Counter Anions

A more subtle chemical influence is the variation of the anion associated with a cationic spin crossover system. In ionic lattices with cationic SCO complex molecules and uncoordinated counter ions in lattice positions remote from the metal center, the anion can nevertheless exercise a strong influence on the SCO behavior through cooperative interactions. These interactions can result in the displacement of the transition temperature, even to the extent that SCO is no longer observed, or may also cause a fundamental change in the nature of the transition, for example from abrupt to gradual. For the $[Fe(2\text{-picolylamine})_3]^{2+}$ salts the degree of completion and steepness of the spin transition curve increases in the order iodide < bromide < chloride (Fig. 8).

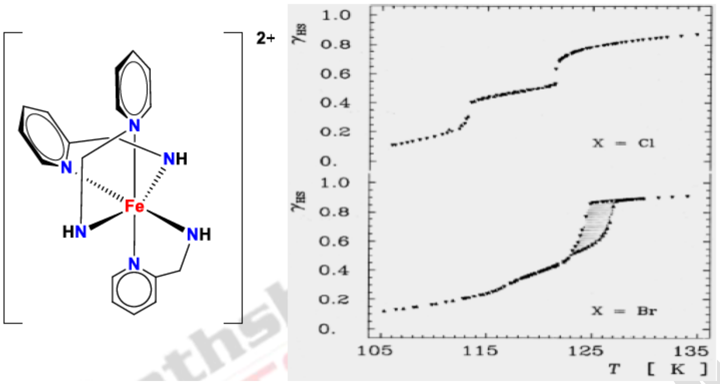
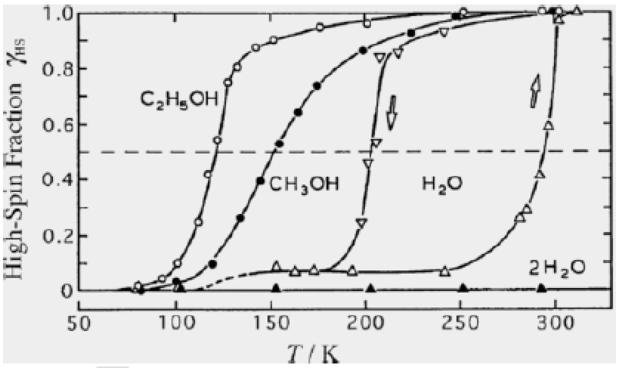


Fig. 8

Effect of Non-Coordinated Solvents Molecules

The nature and degree of solvation of salts or neutral species can also alter the transition temperature. The nature of solvate molecule in $[Fe(pic)_3]Cl_2$ solvent determines the transition temperature. Various solvates of the SCO complexes $[Fe(2\text{-}pic)_3]Cl_2 \cdot$ Solvent with Solvent = EtOH, MeOH, H_2O, $2H_2O$ were studied to explore the influence of the non-coordinated solvent molecules on the SCO behavior. The spin transition curve (Fig. 9) of the complex with solvent ethanol shows a rather steep transition near 115 K; the methanolate shows a more gradual spin transition (ST) near 150 K; the monohydrate and dihydrate exhibits a very broad hysteresis loop with transition temperatures *T* near 200 K and near 290 K, respectively; and the dehydrated sample exhibits no spin transition at all but remains in the LS state.



(Fig. 9)

Effect of Hydrogen bonding

Hydrogen bonding can also impart a major influence on both the transition temperature and the nature of the transition, providing the structural links for communication between the SCO centers. Thus, the extent to which anion or solvate molecules can form hydrogen bond with the SCO center will likely influence the nature of transition. Hydrogen bonding also seems to play a significant role in changes in SCO behavior accompanying hydration/dehydration processes. It has been proposed that hydration will generally result in a stabilization of the LS state, through hydrogen bonding of the water with the ligand. This does indeed seem to be the case for most hydrates, but in a cationic SCO system where the ligand is hydrogen bonded to the associated anion only and this in turn is bonded to the water, the effect can be reverse, i.e. loss of water can also result in stabilization of the LS state.

Effect of Metal Dilution

The effect of dilution of spin transition complexes into the lattice of isostructural species which do not or cannot show SCO has proved to be very diagnostic of the function of cooperative interactions in influencing the nature of spin crossover in solids. This was shown first for the mixed crystal series $[Fe(II)_xZn_{1-x}(2\text{-pic})_3]Cl_2\cdot EtOH$, with x ranging from 0.007 to 1. Zinc was chosen in this "metal dilution" study because it has the same crystal structure as the analogous Fe(II) complex. The transition curve is abrupt for the neat compound (x=1), but becomes increasingly more gradual with increasing dilution, as is generally found for thermal ST in liquid solutions (Fig. 10). Moreover, the transition is shifted to lower temperatures, reflecting increasing stabilization of the high spin state. These results clearly support the existence of cooperative elastic interactions between the SCO metal centers as the transition proceeds. The nature of such cooperative interactions is purely mechanical.

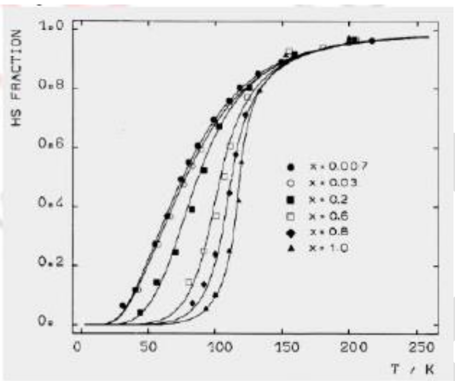


Fig. 10

Physical Factors

Effect of Applied Magnetic Field

As we know that the spin transition phenomenon involves different spin states having different magnetic properties, so the SCO behavior is expected to respond to an applied magnetic field. This indicates a change of the spin transition curve with applied magnetic field. Perturbation of a spin transition by an external magnetic field is predicted by thermodynamics and the magnitude of the change in transition temperature can be calculated if the magnetic response of the molecules involved is known (susceptibility of the two spin states).An experiment with a sample of $[Fe(phen)_2(NCS)_2]$, shows that the transition temperature measured by susceptibility measurements in an applied field of 1 T shifts by −0.11 − 0.04 K when the field is increased to 5.5 T.

Effect of Sample Preparation

Mechanical treatment of samples or different synthetic procedures has been shown to strongly influence the SCO behavior. For instance, ball milling or crushing crystals in a mortar often resulted in the flattening of the ST curve with an increase of the residual high spin fraction in the low-temperature region. The SCO characteristics may also be influenced by the synthetic procedure, as illustrated for $[Fe(phen)_2(NCS)_2]$. This can be prepared in two principal ways: by precipitation from methanol or by extraction with acetone of a phenanthroline molecule from $[Fe(phen)_3](NCS)_2\cdot H_2O$. The samples prepared by both methods have the same chemical formula, but exhibit different SCO behavior. The compound obtained by the first method shows a smooth ST with a significant HS fraction at low temperature, whereas that prepared by the second undergoes a sharp and complete spin transition. The origin of these effects is mainly crystal defects introduced during sample preparation either by milling or rapid precipitation. The particle size has also been reported to play a significant role.

Effect of Pressure

Increase in external pressure shortens the metal–donor-atom distances of SCO complex and increases the ligand field strength at the metal center. It is therefore expected that an increase in the pressure stabilizes the low spin state and increases the transition ctemperature. An increase in pressure on the complex is likely to shift the high spin ↔ low spin equilibrium in favor of the low molecular volume, i.e., towards the low spin form. For example, [Fe(III) (N, N-di-n-butyldithiocarbamate)$_3$] exhibits high spin ↔ low spin equilibrium and the magnetic susceptibility of complex decreases with pressure increasing from 1.013×10^5 to 3.039×10^5 kPa. Since the equilibrium gets shifted from the high-spin $^6A_{1g}$ to the low spin $^2T_{2g}$ form of lower molecular volume. A wide range of paramagnetic Ni^{2+} complexes (high spin) can be converted to the diamagnetic low spin systems by the application of pressure. For example, four coordinated complex, [Ni(II)(N, N-diethylaminotropioneimine)$_2$] (Fig.11) shows an equilibrium between the tetrahedral and square planer species in solution.

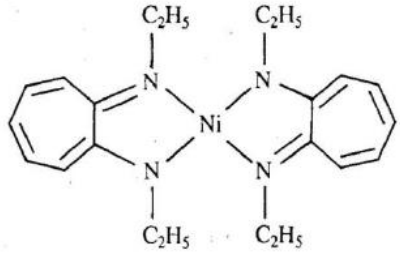


Fig. 11

The tetrahedral form of this complex is paramagnetic ($^3T_1$) and the square planar form is diamagnetic ($^1A_1$). With an increase in the pressure, the proportion of high spin square planar form increases, however, proportion of the high spin tetrahedral form decreases. This results in the decrease of magnetic susceptibility of the sample. From the magnetic moments of high and low spin forms the equilibrium constant at a given pressure can be calculated as follows:

$$\mu_{exp}^2 = \gamma_{HS}\mu_{HS}^2 + \gamma_{LS}\mu_{LS}^2$$

($\gamma_{HS}$is the mole fraction of high-spin species and $\gamma_{LS}$is the mole fraction of low-spin species)

$$\mu_{exp}^2 = \gamma_{HS}\mu_{HS}^2 + (1-\gamma_{HS})\mu_{LS}^2$$

$$\gamma_{HS} = \frac{\mu_{exp}^2 - \mu_{LS}^2}{\mu_{HS}^2 - \mu_{LS}^2}$$

$$\gamma_{LS} = \frac{\mu_{HS}^2 - \mu_{exp}^2}{\mu_{HS}^2 - \mu_{LS}^2}$$

$$Equilibrium\ Constant\ K = \frac{\gamma_{HS}}{\gamma_{LS}} = \frac{\mu_{exp}^2 - \mu_{LS}^2}{\mu_{HS}^2 - \mu_{exp}^2}$$

It is noteworthy to mention that $NiCl_2$ which exists in only one spin state shows no change in its magnetic susceptibility in the pressure range 1.013×10^5 to 3.039×10^5k Pa in water or chloroform.

Quenching of orbital magnetic moment (angular momentum) by crystal field (qualitative approach)

Actual orbital contribution to the magnetic moment of a complex is always less than expected value. The orbital angular momentum for the metal ion is reduced due to the presence of ligands (ligand complexation). Even in some cases, L is effectively zero and the orbital contribution to the magnetic moment is said to be quenched. When significant deviation is observed from μ_S, the orbital contribution becomes significant. For example, in octahedral d^3, d^4 (HS), d^5 (HS), d^6 (LS), d^7 (LS) and

d^8 complexes the quenching of orbital angular momentum is observed. If an electron is to have orbital angular momentum, it must effectively rotate about the axis (preferably z-axis) referred to for the orbital rotation.

The overall magnetic moment is usually given by $\mu_{eff} = g\,[J\,(J + 1)]^{1/2}$. For a free electron S $= \frac{1}{2}$, L = 0 and J $= \frac{1}{2}$, and $g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} = 2$. Due to relativistic correction, $g_J = 2.0023$ for free electrons.

The unpaired electron in a first transition series metal ion is in the 3d orbitals. A transition metal ion has five 3d orbitals all of which are degenerate. For an electron in these orbitals to generate the orbital magnetic moment, the electron should go around the nucleus via these orbitals. For the purpose the following three conditions should be satisfied.

(a) the orbitals should be degenerate.
(b) the orbitals should be of similar shape and size, i.e., they should be transformable by rotation around some axis and
(c) the orbitals must not contain electron of identical spin.

In presence of ligand field, the degeneracy of the d orbitals is partly disturbed. In an octahedral stereochemistry, five d-orbitals split into two degenerate groups viz. t_{2g} and e_g. The $d_{x^2-y^2}$ and d_{z^2} (e_g in O_h or e in T_d) orbitals cannot generate orbital magnetic moment due to non-transformability of $d_{x^2-y^2}$ and d_{z^2} orbitals by rotation. Second condition is not satisfied and the e_g set is known as non-magnetic doublet (in the sense of orbital magnetic moment, contributes nothing to orbital angular momentum), spin magnetic moment continues to be associated with these orbitals. The t_{2g} sets viz. d_{xy}, d_{yz}, d_{zx} (t_{2g} in O_h or t_2 in T_d) orbitals obey the first and second rules. The d_{xz} and d_{yz} orbitals are degenerate and d_{xz} orbital can be transformed to d_{yz} orbital by rotating 90° about z-axis. During such rotation the electron in this orbital is partly orbiting around the nucleus and expected to contribute orbital angular momentum. Herein, the third condition (no electron of identical spin) dictates the contribution of orbital magnetic moment. An octahedral complex with d^1 and d^2 configuration fulfils all the three conditions while d^3 configuration does not satisfy the third condition. Thus, d^1 and d^2 configurations carry the orbital magnetic moment and d^3 configuration lacks the same. Similarly, third condition is also not satisfied in case of t_{2g}^6 (LS d^6) configuration (no contribution to orbital angular momentum). Thus, the occupancy of high spin $d^1(t_{2g}^1)$, $d^2(t_{2g}^2)$, $d^6(t_{2g}^4e_g^2)$, $d^7(t_{2g}^5e_g^2)$ and low spin $d^4(t_{2g}^4)$, $d^5(t_{2g}^5)$ levels are expected to make orbital contribution in octahedral complex

Tetrahedral complexes can be treated in the same way. In this case e level is occupied first and the complexes are mostly high spin. Hence the configurations which are likely to contribute to the orbital contribution are $d^3(e^2t_2^1)$, $d^4(e^2t_2^2)$, $d^8(e^4t_2^4)$, $d^9(e^4t_2^5)$.

Comparison of observed and estimated spin only value of magnetic moment is crucial for predicting the orbital contribution. Except aforesaid configurations, no contribution is observed to the orbital angular momentum for others.

When an electron distribution admits of one arrangement, the corresponding term is singlet (A); when two arrangements are possible, the term is a doublet (E); with three arrangements, the term is triplet (T). In a term symbol, the left-hand superscript denotes the spin multiplicity, the right-hand subscript g indicated gerade (center of symmetry), and the right-hand subscript numerals 1, 2 have the group of theoretical origin. The configurations that contribute nothing to orbital angular momentum possess the A_1 (arising from free ion S term), E (arising from free ion D term) and A_2 (arising from free ion F term) ground state terms. However, ions with t_{2g}^1, t_{2g}^2, t_{2g}^4 and t_{2g}^5 electrons will have T-ground state terms and have some residual orbital contributions.

Table 2: Orbital contribution in octahedral and tetrahedral complexes

d^n	HS Octahedral complex		HS Tetrahedral complex	
	Ground state	Orbital contribution	Ground state	Orbital contribution
d^1	t_{2g}^1 ($^2T_{2g}$)	Expected	e^1 (^2E)	Not Expected
d^2	t_{2g}^2 ($^3T_{1g}$)	Expected	e^2 ($^3A_2$)	Not Expected
d^3	t_{2g}^3 ($^4A_{2g}$)	Not Expected	$e^2t_2^1$ ($^4T_1$)	Expected
d^4	$t_{2g}^3e_g^1$ (^5E_g)	Not Expected	$e^2t_2^2$ ($^5T_2$)	Expected
d^5	$t_{2g}^3e_g^2$ ($^6A_{1g}$)	Not Expected	$e^2t_2^3$ ($^6A_1$)	Not Expected
d^6	$t_{2g}^4e_g^2$ ($^5T_{2g}$)	Expected	$e^3t_2^3$ (^5E)	Not Expected
d^7	$t_{2g}^5e_g^2$ ($^4T_{1g}$)	Expected	$e^4t_2^3$ ($^4A_2$)	Not Expected
d^8	$t_{2g}^6e_g^2$ ($^3A_{2g}$)	Not Expected	$e^4t_2^4$ ($^3T_1$)	Expected
d^9	$t_{2g}^6e_g^3$ (^2E_g)	Not Expected	$e^4t_2^5$ ($^2T_2$)	Expected

The tetrahedral Ni (II), octahedral Co (II) and octahedral Fe (II) complexes have higher magnetic moment than spin only magnetic moment. Further, octahedral Ni (II) and tetrahedral Co (II) are expected to have the spin only magnetic moment, but their magnetic moment is substantially higher. This is because the excited states of Ni (II) ($t_{2g}^5e_g^3$) and Co (II) ($e^3t_2^4$) carry orbital magnetic moment. In a system having such an excited state, spin-orbit coupling brings about some mixing of the ground state with the excited state and thus contributing some orbital contribution.

With the help of the above stated three conditions, it is also possible to predict the possibility of orbital contribution for low spin octahedral complexes. For example, a LS d^5 complex ($^2T_{2g}$) has t_{2g}^5 configuration, and therefore fulfills all the three conditions. But a LS d^7 complex (^2E_g) has $t_{2g}^6e_g^1$ configuration, and has no orbital contribution.

The loss of degeneracy of the orbitals affects the unrestricted motion of electrons about the nucleus. In a stereochemistry of a low symmetry such as tetragonally distorted octahedral complex, a trigonal bipyramidal complex and a square pyramidal complex, the d-orbitals lose their degeneracy to a significant extent. In such complexes, the magnetic moment is close to spin only magnetic moment.

Experimental measurement of Magnetic Susceptibility

Methods for measuring magnetic susceptibilities are based on measuring the force exerted on a substance when placed in an in homogenous magnetic field. This force is proportional to the paramagnetism of the substance, tends to draw the substance toward the more intense part of the field.

Gouy's Method (simplest and most widely used method)

In the Gouy method, a tube filled up to a certain height with the magnetic sample is suspended from an arm of a sensitive balance such that the bottom part of the sample is in a strong magnetic field (in the range 5000-20000 gauss) and the top part is in a zero field. The whole set up is enclosed in such a way that there is no vibrational and air disturbance.

Force, dF experienced by a small volume of the sample, *dv* of volume magnetic susceptibility, κ is given by

$$dF = H\kappa dv(dH/dx) = H\kappa Adx(dH/dx) = H\kappa AdH$$

where, dH/dx is the gradient of the magnetic field, A is the cross-sectional area and dx is the height of the sample

Considering the magnetic field between H and H^o and integrating, we have

$$\begin{aligned} F &= \int dF \\ &= A(\kappa)(1/2)\{H^2 - (H^o)^2\} \\ &= A\,\chi_g(\rho)(1/2)\,)\{H^2 - (H^o)^2\} \qquad \text{(where } \rho \text{ is the density)} \\ &= A\,\chi_g\,(m/v)\,(1/2)\,\{H^2 - (H^o)^2\} \\ &= \chi_g\,(m/l)\,(1/2)\,\{H^2 - (H^o)^2\} \end{aligned}$$

where m and l represent the mass and the length of the sample respectively. If H^o is made negligible, then

$$F = \chi_g[m/(2l)]H^2$$

The force experienced by the sample is measured by the change in its weight. Thus,

$$\chi_g = (2lF/\,mH^2) = (2l \text{ x } \Delta W \text{ x } 981)/\ \{(\text{mass of the sample}) \text{ x } H^2\}$$

where ΔW = change in mass due to imposition of magnetic field

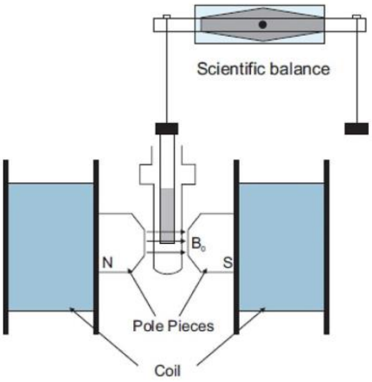


Figure 3: Gouy's magnetic balance

The preceding procedure can be simplified by measuring ΔW of a substance of known magnetic susceptibility, keeping H the same as while measuring ΔW of the sample:

(a) The given tube is weighed first without and after the application of a magnetic field (H) and the difference in mass (Δx) is noted.

(b) The tube is packed upto a height of 10-11 cm with a standard-a paramagnetic or a diamagnetic substance whose X_g is accurately known.

(c) The tube containing the standard is weighed without and then after the application of the same magnetic field (H) as in (a), and the difference in mass (Δy) is recorded. The sum of Δx and Δy gives ΔW_s.

(d) The mass of the standard (W_s) is calculated from the measurement in (a) and (c) without the magnetic field.

(e) The tube is next cleaned and dried. The mass of this empty tube and its mass under influence of the same magnetic field (H) as in (a) are measured, and the difference worked out.

(f) The tube is packed up to same height as in (b) with the magnetic sample being investigated, and the tube is weighed without and after the application of the same magnetic field (H) as in (a)

(g) The mass of the compound (W_c) and ΔW_c is calculated

When $Hg[Co(NCS)_4]$ is used as standard, (χ_g) of the compound can be calculated as

$\chi_g = (\chi_g)_s \times (W_s/\Delta W_s) \times (\Delta W_c/W_c)$,

where $(\chi_g)_s$ is the gram susceptibility of the standard and has a value 16.44×10^{-6} CGS unit at 293 K.

The molar susceptibility (χ_M) is calculated by multiplying χ_g with the molecular weight of the compound. The value so obtained is corrected for the diamagnetism of the ligands, anions, solvents of crystallization, and metal ion, and for the temperature independent paramagnetism (TIP). Thus,

$\chi_M^{corr} = \chi_M$ - diamagnetic correction - TIP

Faraday's method

In this method, a very small volume of the magnetic sample is packed in a quartz ampoule with an internal diameter of about 1mm and suspended from a sensitive balance is placed in a region of reasonably strong magnetic field so that the product $H(dH/d\chi)$, where $dH/d\chi$ is the gradient of the field, is constant over the volume of the sample. The whole set up is housed in enclosure which can be flushed with nitrogen or helium. The region of uniform $H(dH/d\chi)$ is determined by placing a small volume of a calibrant of mass m and of known magnetic susceptibility at different points along the field. The value of $H(dH/d\chi)$ is obtained from the relation

$dF = m\chi_g H(dH/d\chi)$ or $H(dH/d\chi) = dF/(m\chi_g)$

where dF is the force experienced by the sample due to magnetic field and is measured using a cathetometer. With the help of the measurements first with a calibrant and then with the sample, we have

$\chi_s = \chi_c(d_s/d_c)(m_c/m_s)$

Where χ_s and χ_c are the susceptibilities of the sample and the calibrant, m_s and m_c are the respective masses, and d_s and d_c are the respective deflections at constant $H(dH/d\chi)$

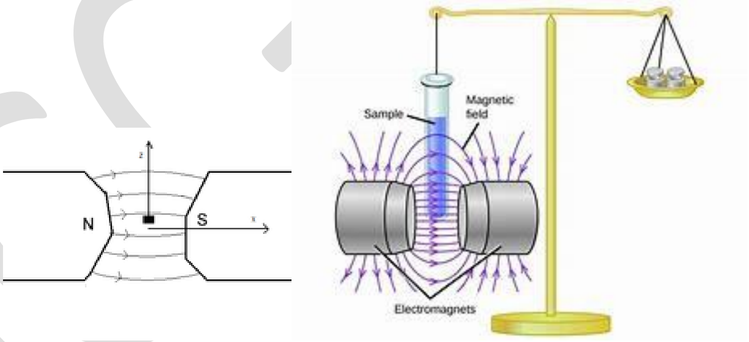


Figure 5: Faraday method for determining the magnetic susceptibility.

NMR method

It is based on the principle that the position of proton resonance line of a compound is dependent on the bulk susceptibility of the medium in which the compound is placed. Here a concentric cell of length >> diameter is used. The inner tube of the cell contains an aqueous solution of the paramagnetic substance whose magnetic susceptibility is to be determined and about 3% tert-butanol as the inert standard. In the annular section of the cell, an identical solution without paramagnetic substance is placed. The paramagnetic substance shifts the proton resonance lines of the standard (i.e., tert-butanol) and as a result, two resonance lines are observed for the methyl protons of tert-butanol. The shift is given by the expression

$\Delta H = (2\pi/3)\Delta V \times H$

where H is the applied magnetic field and $\Delta V = V_s - V_0$, V_s and V_0 being the volume magnetic susceptibility of the solution and the solvent respectively. The gram susceptibility of the paramagnetic substance is calculated from the equation

$$\chi_g = \chi_0 + \{\chi_0(\rho_o-\rho_s)/m\}(3/2\pi m)\ (\Delta H/H)$$

Where χ_0 is the gram susceptibility of the solvent, m is the mass of the paramagnetic substance contained in 1ml of the solution, and ρ_o and ρ_s are the density of solvent and the solution respectively.

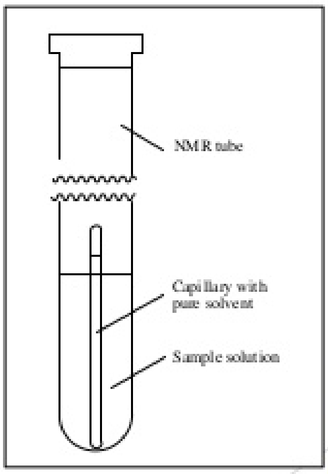


Figure 5: Concentric NMR tube for measuring magnetic susceptibility in solution.

In this method, 1% TMS or 1% benzene can also be used as the standard
The comparisons of the three are tabulated below:

Methods	Advantages	Disadvantages
Gouy	Robust equipment, good sensitivity, convenient solution measurements	Packing error of about 3-5%, large amount of sample required
Faraday	Small amount of sample required, good sensitivity	Delicate equipment, fragile suspension devices, constructional difficulty, inconvenient solution measurement, small weight changes
NMR	Good sensitivity, small amount of (about 0.2 ml) required, speedy and simple measurement, temperature can be controlled and varied	Measurements in solution only, NMR spectrometer essential.

Magnetochemistry-Part III

Magnetic Susceptibility – Van Vleck Equation

The magnetic susceptibility of a paramagnetic substance originates from the paramagnetic dipoles present in it. On application of a magnetic field,

1) The magnetic dipoles tend to align themselves along the field direction against the disrupting influence of the temperature. As a result, M_J levels (of a particular J) are symmetrically split into lower and upper levels. This splitting is known as first order Zeeman Effect.

2) The orbitals get distorted via the introduction of some character of the excited state in the ground state. This is known as second order Zeeman Effect.

Derivation

Derivation of Van Vleck Equation involves two assumptions viz. the paramagnetic susceptibility is independent of the applied magnetic field (H), and the energy of the ith level of the atom/ion is a power series in H i.e.,

$$W_i = W_{i(0)} + W_{i(1)}H + W_{i(2)}H^2 + ... \qquad (1)$$

where, $W_{i(0)}$ is the energy of level n in zero applied field (absence of H), $W_{i(1)}$ and $W_{i(2)}$ are the first-order second-order Zeeman coefficient respectively. Expansion of the energy to the second-order is usually sufficient. The first term, $W_{i(0)}$ makes no contribution to the moment of a given state. If a substance is devoid of permanent magnetic dipoles, then there is no first order Zeeman interaction with H and hence $W_{i(1)}$ is zero.

A magnetic dipole, on interacting with magnetic field lowers its energy by $-\mu H$. Thus, by differentiating $W = -\mu H$ with respect to H, we have

$$\mu = -\delta W/\delta H \qquad (2)$$

Considering the ith level, we have

$$\mu_i = -W_{i(1)} - 2W_{i(2)}H \text{ (neglecting the higher terms)} \qquad (3)$$

Assuming several states each having characteristic μ_i and considering its average μ_{av} we have

$$\chi_M = N\mu_{av}/H \qquad (4)$$

where, $\mu_{av} = \Sigma n_i\mu_i/N \qquad (5)$

The population of the levels is thermally controlled by Boltzmann's law and thus,

$$n_i = n_o\exp[-W_i/(kT)] \qquad (6)$$

where n_i and n_o represent the number of molecules in the ith level and the ground state level, respectively.

Again,

$$\exp[-W_i/(kT)] = \exp[\{-W_{i(0)} - W_{i(1)}H - W_{i(2)}H^2\}/kT]$$
$$= \exp[-W_{i(0)}/kT]\exp[\{-W_{i(1)}H - W_{i(2)}H^2\}/kT] \qquad (7)$$

Compared to kT, the splitting of energy levels due to first order Zeeman effect is very small and second order Zeeman splitting is also less. When x is small, exp(-x) ~ (1-x). Thus,

$$\exp[-W_i/(kT)] = \exp[-W_{i(0)}/kT]\,[\{1 - W_{i(1)}H/kT\}\{1 - W_{i(2)}H^2/kT\} \qquad (8)$$

Thus,

$$\mu_{av} = n_o\,\Sigma\mu_i\exp[-W_i/(kT)]/n_o\exp[-W_i/(kT)] \qquad (9)$$

Since, $N = \Sigma\, n_i = n_o\exp[-W_i/(kT)]$. Taking the value of μ_i from equation (3) we have

$$\mu_{av} = \Sigma[(-W_{i(1)} - 2W_{i(2)}H)]\exp[(-W_{i(0)}/(kT)]\,[(1 - W_{i(1)}H/(kT)]/\exp[(-W_{i(0)}/(kT)]\,[(1 - W_{i(1)}H/(kT)] \qquad (10)$$

Since, the first order Zeeman effect splits a level symmetrically above and below the zeroth level, $\Sigma W_{i(1)} = 0$ and hence, $\Sigma W_{i(1)} \exp[(-W_{i(0)}/(kT) = 0$ (11)

The equation (10) reduces to

$$\mu_{av} = H\{\Sigma_i[(W_{i(1)})^2/kT - 2(W_{i(2)})]\exp(-W_{i(0)}/(kT)\}/\{\Sigma_i \exp(-W_{i(0)}/(kT)\} \quad (12)$$

The magnetic susceptibility, χ_M is given by

$$\chi_M = M/H = N\{\Sigma_i[(W_{i(1)})^2/kT - 2(W_{i(2)})]\exp(-W_{i(0)}/(kT)\}/\{\Sigma_i \exp(-W_{i(0)}/(kT)\} \quad (13)$$

This is the usual form of the Van Vleck equation, the magnetic susceptibility is determined by taking a population weighted average of the susceptibility of a specific level. When $W_{i(0)}$ is zero, the above equation reduces to (by replacing the summation term by the multiplicity of the J level)

$$\chi_M = N\{\Sigma[(W_{i(1)})^2/kT - 2(W_{i(2)})]/\text{multiplicity of the J level} \quad (14)$$

This is known as simplified Van Vleck equation.

Simplification of Van Vleck equation:

(a) In zero field, there is only one energy level, and this is degenerate

In this case $W_{i(2)} = 0$ since there is no set of levels j with which to interact. Further, our reference energy level is $W_{i(0)}$, which can be considered to be zero, therefore $\exp(-W_{i(0)}/kT) = 1$. Equation (13) then becomes

$$\chi_M = N\{\Sigma_i(W_{i(1)})^2/kT\}/n \quad (15)$$

where, n is the degeneracy of the level.

For a particular case, $\Sigma_i(W_{i(1)})^2$ is a constant (say C) and we can write

$$\chi_M = C/T \quad (16)$$

Equation (16) is the Curie law.

The effective magnetic moment, μ (if it obeys Curie law) is thus given by

$$\mu = 2.828\,(\chi_M T)^{1/2} = 2.828\,C^{1/2} \quad (17)$$

Thus, μ is independent of temperature is the susceptibility obeys Curie law. The plot of $1/\chi_M$ vs T is a straight line passing through the origin

Although, the Curie law may be approximately obeyed in many cases, no transition metal complex exists which has only one energy level in zero field. Hence, this condition has no direct practical application

(b) The ground term is a singlet, and there is at least one degenerate excited state but these are all >> kT above the ground state

In this case $W_{i(1)}$ is zero since the level i is a singlet, thus we can use $W_{i(1)} = 0$ and $\exp(-W_{i(0)}/kT) = 1$. Further, although $W_{j(1)}$ may well be finite, $\exp(-W_{j(0)}/kT)$ will be approximately zero since $W_{j(0)} >> kT$ (level j is not thermally populated) and so there will be no first order Zeeman contribution to χ_M. The only finite term in equation (15) is thus $W_{i(2)}$ and in this case

$$\chi_M = N\{\Sigma_i(W_{i(2)}) = N\alpha \quad (18)$$

The form of $W_{i(2)}$ is given above: it only depends on the separation $(W_{i(0)} - W_{j(0)})$ hence in this situation χ_M is constant (independent of temperature). This is the origin of temperature independent paramagnetism (TIP). When a TIP is observed, it is χ_M and does not depend on the temperature. The magnetic moment derived from a TIP will be function of $T^{1/2}$.

This is a real situation, and is the origin of the paramagnetism of such d^0 systems as the permanganate or chromate ions. In most cases, $(W_{i(0)} - W_{j(0)})$ is large, hence TIP is small (~100 x10^{-6} cgs). In other cases, the TIP may be quite large (like octahedral d^1). $(W_{i(0)} - W_{j(0)})$ becomes smaller, the TIP behaviour merges smoothly into a Curie law behaviour.

(c) The ground state is degenerate and all excited states are >> kT above this

This simply the sum of first two cases. Thus,

$$\chi_M = C/T + N\alpha \qquad (19)$$

Nα is small and when T is further small, the Curie law contribution will be very large. Hence at low temperature a Curie law will be obeyed: χ_M vs 1/T plot will be a straight line passing through the origin, but slightly concave towards the T axis at high temperatures. The magnetic moment will be independent of temperature, apart from small increase at higher temperatures.

This is a real situation and will be observed in any complex with Oh or Td symmetry for which the ground state term is of A or E symmetry. This is because the first excited term will be 10Dq above the ground term (say 10000 cm^{-1}), and the ground terms are not split by spin-orbit coupling so that there is no low-lying excited state (Fig). An approximate value for Nα can be obtained by finding the constant which must be subtracted to bring the $1/\chi_M$ vs T plot to a straight line.

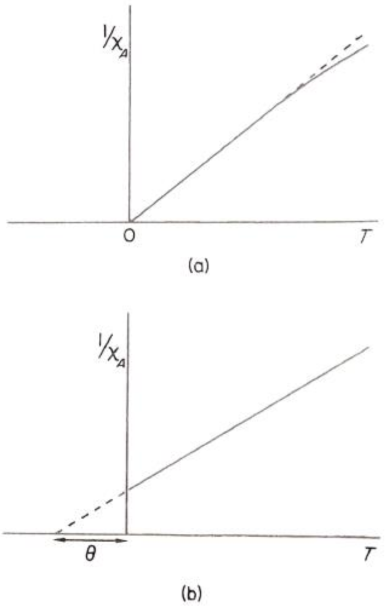


Figure 1.3. Inverse magnetic susceptibility *vs.* temperature for transition complexes: (a) for an ion with an *A* or *E* ground term; (b) for an ion with a *T* ground term.

(d) The ground term is degenerate and there are thermally accessible degenerate excited terms

In this case, $W_{i(0)} = 0$, i.e., exp $(-W_{i(0)}/kT) = 1$. But, both $W_{j(1)}$ and $W_{j(2)}$ are finite as well as $W_{i(1)}$ and $W_{i(2)}$. and in this case, exp $(-W_{j(0)}/kT)$ is not negligible (no simplification of Van Vleck equation). Thus, a complicated temperature dependence of the susceptibility is expected. In practise, the susceptibility obeys a Curie-Weiss law:

$$\chi_M = C/(T + \theta) \qquad (20)$$

where, θ is a Weiss constant.

In these cases, the magnetic moment will depend on temperature. If equation (20) is obeyed, a plot of $1/\chi_M$ vs T will be straight line, but with a finite intercept on the temperature axis. This situation is illustrated in Fig.

There is considerable misunderstanding about the significance of Weiss constant (θ). In most cases, at sufficiently high temperatures magnetic susceptibilities of ferromagnets and antiferromagnets obey Curie-Weiss laws with θ, respectively negative and positive and the above equation becomes

$$\chi_M = C/(T - \theta) \qquad (21)$$

This is the source of confusion. Further, in a magnetically concentrated compound there is some relationship between the magnitude of θ and strength of the magnetic interaction (do follow this if θ is finite, some magnetic interaction exists). Thus, isolated regular octahedral d^1 complexes obey Curie-Weiss law with $\theta \approx 200K$. Some authors also calculate μ value from the expression

$$\mu = 2.828[\chi_M\ (T+ \theta)^{1/2}]$$

For a magnetically dilute solution the above equation cannot be used. Instead, $\mu = 2.828\ (\chi_M T)^{1/2}$ is used.

The behaviour predicted by this case (d), may be expected for any transition metal complex which has a T-symmetry ground term (split by spin-orbit coupling). The resulting states are split by a few hundred wave numbers and thus will be thermally populated. These compounds will have temperature dependent magnetic moments. Thus, the cases (c) and (d) are the basis of the much-used criterion of stereochemistry based upon the temperature dependence or otherwise of the magnetic moment.

Van Vleck Equations

Using quantum mechanics, Van Vleck derived the analogous expression considering the two Zeeman effects

$$\chi_M = N\mu_B^2/3kT + N\alpha \qquad (1)$$

where μ_B^2 is the square of the low frequency part of the magnetic moment vector, averaged over time, and this average being itself averaged over various normal states appropriately weighted according to the Boltzmann factor. Nα is the combined temperature independent contribution of the high frequency elements of the paramagnetic moment, and diamagnetic part. A convenient unit of atomic magnetic moment is the Bohr magneton, the magnitude of which is given by $\beta = eh/4\pi mc = 0.917x10^{-20}$ erg/oersted.

Now equation no (1) becomes

$$\chi_M = N\left(\frac{\beta^2\mu_B^2}{3kT} + \alpha\right) \qquad (2)$$

Where μ_B^2 is the low frequency part of the magnetic moment expressed in Bohr magnetons. In general, the magnetic moment of an atom consists of two parts

1. The orbital contribution, and
2. The electron spin contribution

In different normal states of the atom the inclination of orbital and spin contributions may be different. For many cases, the "permanent" magnetic moment is not invariant with temperature although it appears to be so. Also, "molecular" paramagnetism as contrasted with "atomic" paramagnetism, the orbital contribution appears to be quenched out for most of the cases. In evaluating μ_B^2 and α in terms of experimentally determinable quantities there are three cases for which different equations are required. A multi-electron system possesses several J levels; the ground state J being decided by Hund's rule. The J levels of a given Russell-Saunders term together constitute a multiplet, and given J level is called a component of the multiplet. The energy gap between two successive J levels is known as the multiplet width. Normally, the magnetic property of a substance originates from its ground state. But this is not so when excited states lie close to the ground state, i.e., when the multiplet width is about kT, the thermal energy. In such a situation, the excited state or states may be significantly populated as, for example, in Sm(III) and Eu(III). Therefore, when deriving the magnetic moment equation, we need to also consider the population of the excited states. Such a consideration leads to three distinct situations, (Fig. 1)

1. The multiplet width is large as compared to kT
2. The multiplet width is small as compared to kT
3. The multiplet width is comparable to kT.

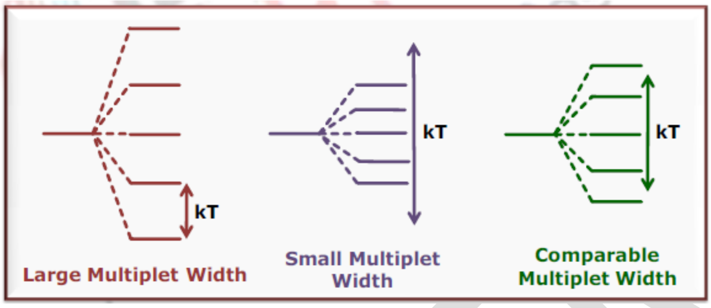


Fig. 1

Multiplet Intervals Large Compared to kT

When the multiplet width is greater than kT, the L and S vectors interact strongly. This means that these vectors process rapidly about the direction of the resultant J vector. In this situation, J becomes good quantum number such that the quantum numbers L and S no longer dictate the ultimate magnetic properties. Therefore, magnetic moment is given by

$$\mu_J = \sqrt{J(J+1)}\, g\beta \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where, following the usual spectral notation, J is the vector sum of L and S; g, the Lande splitting factor is given by

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)} \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

From equation 3, we get the equations for μ_L and μ_S easily. For orbital magnetic moment only, S=0, so that J= L and hence g=1. Therefore,

$$\mu_L = \sqrt{L(L+1)}\,\beta \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

For spin magnetic moment only, L=0, so that J = S and hence g=2. Therefore,

$$\mu_S = \sqrt{4S(S+1)}\,\beta \; \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Equation (2) then becomes

$$\chi_M = \frac{Ng^2\beta^2 J(J+1)}{3kT} + N\alpha \ldots\ldots\ldots\ldots (7)$$

The term α no longer has the value zero (neglecting the diamagnetic part) but is given by

$$N\alpha = \frac{N\beta^2}{6(2J+1)}\left[\frac{F(J+1)}{h\nu(J+1;J)} - \frac{F(J)}{h\nu(J+1;J)}\right] \ldots\ldots\ldots\ldots\ldots (8)$$

Where $F(J) = \frac{1}{J}[(S+L+1)^2 - J^2][J^2 - (S-L)^2] \ldots\ldots\ldots\ldots\ldots (9)$

Equation (3) is used to evaluate the magnetic moment for most of the rare earth ions, elements and susceptibility of the same can be calculated by using equation (7).

Multiplet Intervals Small Compared to kT

When the multiplet width is quite small as compared to kT, virtually all the j levels may be assumed to be populated. Therefore,

$$\mu = \sqrt{4S(S+1)+L(L+1)}\,\beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots(10)$$

The magnetic moment arises from the sum total of the spin and orbital effects. Remembering that the magnetic susceptibility is additive and that the square of magnetic moment is additive. Moreover, the high-frequency elements of the paramagnetic moment are absent (neglecting the diamagnetic part). Equation (2) then becomes

$$\chi_M = \frac{N\mu_L^2}{3kT} + \frac{N\mu_S^2}{3kT} \ldots\ldots\ldots\ldots\ldots\ldots(11)$$

$$\chi_M = \frac{N}{3kT}(\mu_L^2 + \mu_S^2) \ldots\ldots\ldots\ldots\ldots(12)$$

$$\chi_M = \frac{N\beta^2}{3kT}[4S(S+1)+L(L+1)] \ldots\ldots\ldots\ldots\ldots(13)$$

where S and L are the resultant spin and orbital moments respectively. Therefore,

$$\mu_{L+S} = \sqrt{4S(S+1)+L(L+1)}\,\beta \ldots\ldots\ldots\ldots(14)$$

Multiplet Intervals Comparable to kT

When the multiplet width is comparable to kT, then, to calculate the total magnetic susceptibility, it is advisable that the magnetic susceptibility due to each J level, along with the population of the J level, to be considered. This case involves summation of the contributions of atoms with different values of J. The number NJ, that is the number of atoms in a mole with a given value of J, is determined by the Boltzmann temperature factor. The Avogadro number N, is composite of N_J, N_{J+1},…….. Thus, $\chi_M$is given by

$$\chi_M = \sum \frac{N_J g^2\beta^2 J(J+1)}{3kT} + N_J\alpha_J \ldots\ldots\ldots\ldots\ldots(15)$$

Each J level has as many as (2J+1) orientations, we have, for a J level having an energy E above the ground state J.

$$N_J = C(2J+1)e^{\frac{-E}{kT}}$$

Where C is proportionality constant. Substituting the value of $N_J$in equation (15), we get

$$\chi_M = C\frac{\sum_{J=|L-S|}^{L+S}\left\{\left[g_J^2\beta^2 J(J+1)(2J+1)e^{\frac{-E}{kT}}\right]\right\}}{3kT} + C\sum(2J+1)e^{\frac{-E}{kT}}\alpha_J \ldots\ldots\ldots\ldots\ldots\ldots(16)$$

Since $N = \sum N_J = C\sum(2J+1)e^{\frac{-E}{kT}}$, Therefore,

$$C = \frac{N}{\sum(2J+1)e^{\frac{-E}{kT}}}$$

Thus, the final expression for χ_M is given by

$$\chi_M = \frac{N\beta^2}{3kT}\frac{\sum_{J=|L-S|}^{L+S}\{[g_J^2 J(J+1)]+\alpha_J\}(2J+1)e^{\frac{-E}{kT}}}{\sum(2J+1)\,e^{\frac{-E}{kT}}} \ldots\ldots\ldots\ldots\ldots(17)$$

Therefore, magnetic moment is given by

$$\mu = \sqrt{\frac{\sum_{J=|L-S|}^{L+S}\{[g_J^2\beta^2 J(J+1)] + \alpha_J\}(2J+1)e^{\frac{-E}{kT}}}{\sum(2J+1)\, e^{\frac{-E}{kT}}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

It is clear from the above discussion that when the multiplet intervals are small or large compared to kT the Curie law should be obeyed, except for the relatively small temperature independent high frequency elements. But where multiplet intervals are comparable to kT we get a Boltzmann distribution of various "normal" states together with some rather striking departures from the Curie law.

Extra

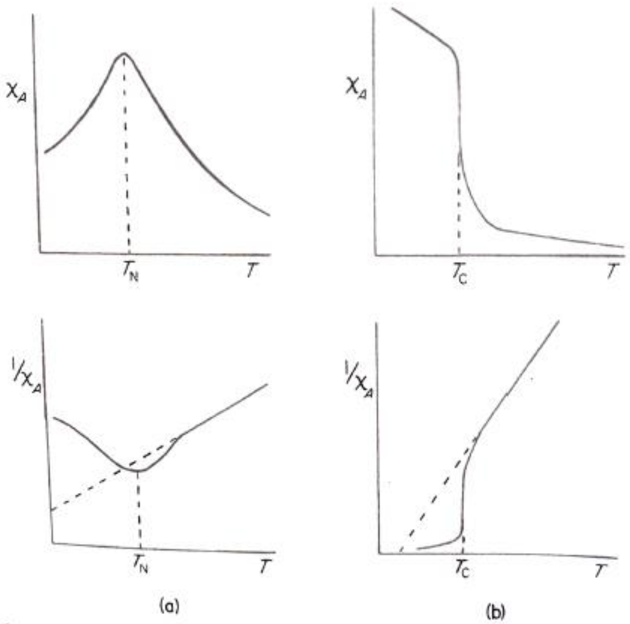


Figure 1.1. Variation of magnetic susceptibility and inverse magnetic susceptibility with temperature: (a) for an antiferromagnetic compound; (b) for a ferromagnetic compound.

Magnitude of magnetic moments (multiplet width large as compared to kT)

When studying the magnetism of a coordination compound, two perturbations viz. one due to the magnetic field and other due to spin-orbit coupling are to be considered.

VanVleck susceptibility equation is given by

$\chi_M = M/H = N\{\Sigma_i[(W_{i(1)})^2/kT - 2(W_{i(2)})]\exp(-W_{i(0)}/(kT)\}/\{\Sigma_i \exp(-W_{i(0)}/(kT)\}$ (1)

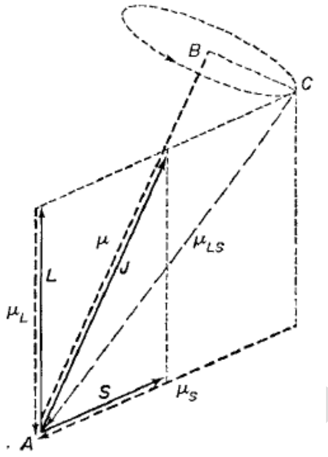
where, N is the one mole of atoms, $W_{i(0)}$ is the energy of level n in zero applied field, and $W_{i(1)}$ and $W_{i(2)}$ are the first-order second-order Zeeman coefficient respectively. k is Boltzmann constant and T is the temperature.

Let us examine the perturbation by magnetic field. The first order perturbation effect (or Zeeman coefficient) is an integral of the type $\int \psi i * \mu\psi i\, d\tau$ where ψ_i is the wave function of a level which is degenerate in zero field, μ is the appropriate magnetic moment operator. If $W_{i(1)}$ is finite, the level i is split into a set of equally spaced components separated by gβH. The susceptibility arises from the changes in energy on thermal population of these new states.

Neglecting the second order Zeeman effect i.e., using $W_{i(2)} = 0$ in equation (1) we have

$\chi_M = M/H = N\{\Sigma_i[(W_{i(1)})^2/kT\,]\exp(-W_{i(0)}/(kT)\}/\{\Sigma_i \exp(-W_{i(0)}/(kT)\}$ (2)

When multiplet width is large, L and S are not good quantum number, instead J is. For orbital and spin magnetic moments, g is 1 and 2 respectively. For quantum number J, it is represented as g_J.



The coupling of *L* and *S* and the associated magnetic moments

The components of *L* and *S* in the direction of J are respectively Lcos (LJ) and Scos (LJ). Using the cosine rule

$$S^2 = J^2 + L^2 - 2LJ\cos(LJ)$$

$$L^2 = J^2 + S^2 - 2SJ\cos(SJ)$$

$$\therefore \quad L\cos(LJ) = \frac{J^2 + L^2 - S^2}{2J}$$

$$S\cos(SJ) = \frac{J^2 + S^2 - L^2}{2J}$$

The effective resultant moment, μ, is the sum of the moments associated with these component angular momenta. The magnetic moment operator then (using above) is given by

$\mu_J = \beta L\cos(LJ) + 2\beta S\cos(SJ) = g_J\beta H$ (3)

At ground state in absence of magnetic field, $W_{i(0)} = 0$ and equation (2) reduces to

$\chi_M = M/H = N\{\Sigma_i[(W_{i(1)})^2/kT\,]\}/\{\Sigma_i \exp(-W_{i(0)}/(kT)\}$ (4)

The first order Zeeman effect for the J level is given by

$W_{i(1)}H = M_J g_J \beta H$ (5)

Each J level has multiplicity 2J+1, and equation (4) can be written as

$$\chi_M = \frac{N \sum\limits_{M_J=-J}^{J} M_J^2 g_J^2 \beta^2/(kT)}{2J+1} = \frac{Ng_J^2\beta^2}{kT}\frac{1}{2J+1}\sum_{M_J=-J}^{J} M_J^2$$

$$= \frac{Ng_J^2\beta^2}{kT}\frac{1}{2J+1}2[J^2 + (J-1)^2 + \ldots + 0^2]$$

$$= \frac{Ng_J^2\beta^2}{kT}\frac{1}{2J+1}\frac{2J(J+1)(2J+1)}{6} = \frac{N\beta^2}{3kT}g_J^2 J(J+1).$$

Thus, $\chi_M = N\beta^2 g_J^2\{J(J+1)\}/3kT$ (6)

Again, $\chi_M = N\beta^2\mu^2/3kT$

Or, $\mu = [3kT\chi_M/N\beta^2]^{1/2}$ (7)

Using equation (6) in equation (7) we have

$$\mu_J = g_J[J(J+1)]^{1/2}\beta \quad (8)$$

where μ_J stands for the magnetic moment due to quantum number J
and $g_J = 3/2 + [(S(S+1)-L(L+1)]/[2J(J+1)]$

Magnetochemistry- Part IV

Antiferromagnetism and antiferromagnetic interaction

In an antiferromagnetic substance, the neighbouring magnetic centres are opposed to each other, but in ferromagnetic substance, they are aligned parallel. For antiferromagnetic substances, the neighbouring spins align anti-parallel with one another below a certain critical temperature (T_N, Néel temperature) and below T_N the material tends to remain spin aligned and has a lower moment than expected. The coupling forces are responsible for the alignment of the magnetic spins. Spontaneous alignment of the magnetic dipoles in ferro-/antiferromagnetic states needs some positive energy of interaction between the neighbouring spins. The origin of this coupling is quantum mechanical. Antiferromagnetic interactions can
be divided into two categories.

1. Intramolecular Antiferromagnetism
2. Intermolecular Antiferromagnetism

Intramolecular Antiferromagnetism

Intramolecular antiferromagnetism arises when the interacting paramagnetic centres are situated within the same molecule. In other words, intramolecular antiferromagnetic exchange occurs between two or more centres within the same molecule (necessarily dimeric or polymeric). It is often associated with direct metal-metal bonding between the magnetic centres. The common example of this class is copper (II)acetate monohydrate dimer, $[Cu_2(OAc)_4].(H_2O)_2$. The copper centres in this complex are antiferromagnetically coupled resulting in diminishing of the magnetic moment near 90K. $[Cu_2(OAc)_4].(H_2O)_2$ is essentially diamagnetic due to the cancellation of two opposing spins. For this complex, the room temperature magnetic moment per Cu^{2+} ion is 1.4 B.M., however, if there were no antiferromagnetic interaction, the magnetic moment would have been at least 1.73 B.M.

Another example is $K_4[Ru_2OCl_{10}]$ or $K_4[Cl_5Ru{-}RuCl_5]$. The monometallic low spin d^4 Ru(IV) complex is expected to have two unpaired spin. But the complex $K_4[Ru_2OCl_{10}]$ is diamagnetic due to the coupling of the neighbouring spins leading to the antiferromagnetic exchange.

One more interesting example is d^1 molybdenum(V) complex of ethyl xanthate. This complex is also diamagnetic due to the coupling of the neighbouring spins leading to antiferromagnetic exchange. If there were no antiferromagnetic interaction, the magnetic moment of the complex would have been 1.73 B.M. per Mo^{5+}.

Intermolecular Antiferromagnetism

Intermolecular antiferromagnetism arises due to the exchange between many centres in a crystal lattice. In other words, intermolecular antiferromagnetic exchange occurs between two or more centres within different molecules in a crystal lattice. The transition metal oxides and halides belong to this class, e. g., perovskite fluorides, KMF_3, where M (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} etc.) stands for almost any bivalent transition metal ion. A weak intermolecular antiferromagnetic coupling occurs in many transition metal complexes. The extent of such an effect may be checked by measuring the magnetic susceptibility in solution where it should be poorer than in the solid state

Antiferromagnetic Exchange Pathways: Mechanisms of antiferromagnetic exchange interaction

Antiferromagnetic interaction involves the interaction between electronic spins on neighboring metal atoms. The mechanism of the exchange interaction involves the mutual pairing of electron spins via some form of orbital overlap, analogous to the formation of a chemical bond. The following two mechanisms are usually used to account for antiferromagnetic exchange viz. direct interaction (direct metal-metal interaction via the overlap of suitable metal orbitals) and superexchange (the transfer of paramagnetic spin density from one metal ion through the orbital overlap of the diamagnetic bridging atoms to an adjacent metal ion, involves three atoms)

Direct interaction

This mechanism involves direct overlap between the orbitals containing the unpaired electrons, leading to mutual pairing in the ground state. This mechanism is the one considered to be responsible for exchange interaction in Cu(II)acetate monohydrate. Herein, weak overlap between the dx^2-y^2 orbitals on each Cu-atom, giving a δ-bond (Fig. 1) This weak overlap leads to a diamagnetic spin-singlet ground state for the molecule.

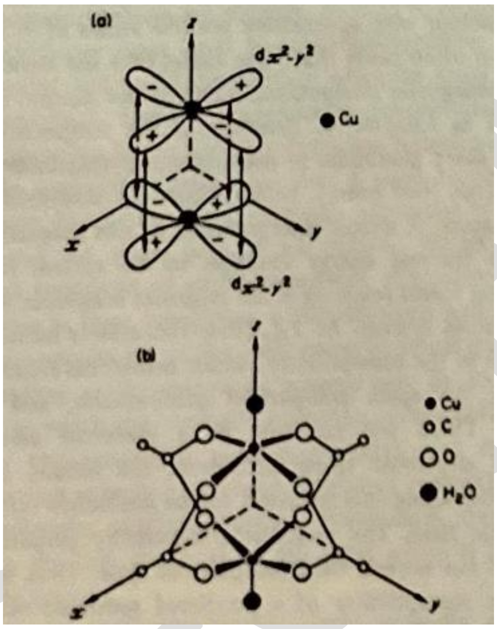


Fig 1: (a) An illustration of the δ-bonding in and (b) the structure of Cu(II)acetate monohydrate

In addition, the interaction also gives rise to an excited paramagnetic spin-triplet state. The observed magnetic behavior arises from thermal population of the spin-triplet state (Fig. 2) The overlap between the metal dx^2-y^2 orbitals is relatively weak, not considered to be responsible for holding the molecule together, and in the normal sense it would not be considered to constitute a metal-metal bond.

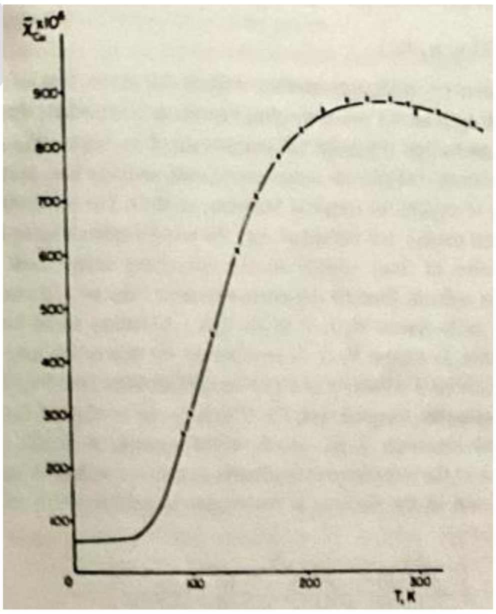


Fig. 2: The variation in χ_{Cu} with T for Cu(II)acetate monohydrate

More extreme examples of the direct interaction involving transition metal d-orbitals occur in carbonyl and halide cluster compounds. For example, in $(CO)_5Mn\text{-}Mn(CO)_5$ there is considered to be a strong overlap between Mn d-orbitals, which formally may be expected to contain an unpaired electron in the monomer (Fig 3). This overlap leads to a metal-metal bond which is responsible for holding the molecule together and pairs the odd electrons leading to a diamagnetic ground state for the molecule

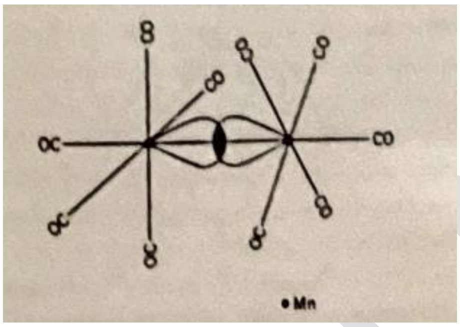


Fig. 3: An illustration of metal-metal bonding in $Mn_2(CO)_{10}$

Superexchange

This mechanism for antiferromagnetism involves the interaction of electrons with opposite spins on the two interacting ions via an intermediate diamagnetic anion. This mechanism is usually the one postulated to explain the antiferromagnetism of oxide and fluoride lattice compounds and was first proposed by Kramers to explain the magnetic behavior of MnO. The mechanism again involves orbital overlap, but instead of only the metal d-orbitals being involved, the participation of filled orbitals on the intervening anion must also be considered. To illustrate this mechanism fully we will consider the hypothetical oxide system M_2O, in which M is a transition metal ion with a single d-electron. In a linear M–O–M arrangement the interaction may occur in two ways; either via a σ-bonding or a π-bonding mechanism (Fig. 4). The σ-bonding mechanism is represented in Fig 4(a), by the overlap of d_{z^2} orbitals on the metal ions with a p_z orbital on the oxygen. A simple pictorial representation of the exchange process involves an electron with spin 'up' on M_1 pairing with one of the electrons in the oxygen p_z orbital which has a spin 'down'. This leaves the other electron in the oxygen p_z orbital with a spin 'up'. If this electron interacts with the electron on M_2 in an antiferromagnetic sense then the electron in the d_{z^2} orbital on M_2 must have its spin 'down'. Similar considerations can be applied to the superexchange mechanism via π-bonding [Fig 4(a)]. These rather crude pictorial representations enable us to envisage how the spins on the interacting metal ions may be aligned in opposite directions and how they may become effectively paired leading to a minimum number of unpaired spins in the ground state of the system.

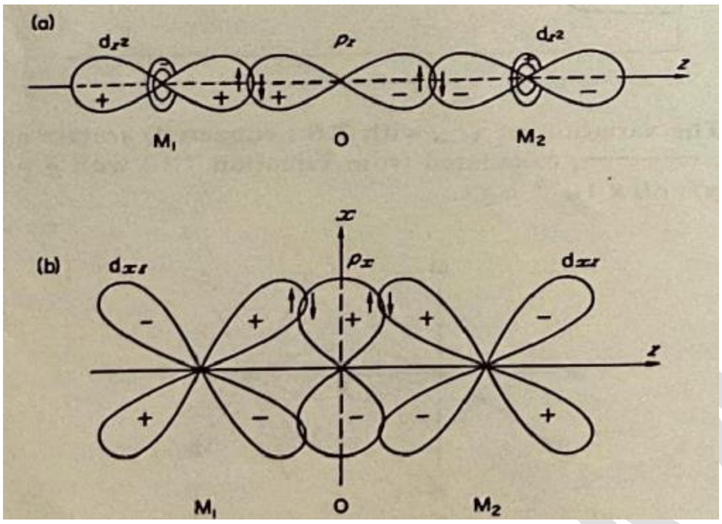
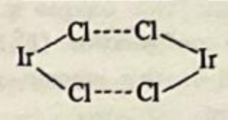


Fig. 4 Superexchange in a linear M-O-M system via (a) σ-bonding (b) π-bonding

The superexchange mechanism just described may be extended to systems in which more than one anion intervenes between the paramagnetic ions. This type of mechanism has been proposed to explain the antiferromagnetic interaction which occurs in certain salts of the $IrCl_6^{2-}$ anion. The exchange between nearest neighboring iridium atoms occurs via two intervening chloride ions in a system of the form



The superexchange model proposed by Kramers was further developed by Anderson in 1950. In the same year, Goodenough and Kanamori proposed some semi-empirical rules for superexchange interaction between these ions. These cumulative rules for a superexchange interaction are called Goodenough-Kanamori-Anderson (GKA) rules.

Statement of the GKA rule (Goodenough-Kanamori-Anderson rule):
(a) 90° superexchange leading to a F-interaction: A 90° superexchange interaction, i.e., magnetic ion-bridging ligand atom-magnetic ion angle=90°) interaction leads to a weak ferromagnetic (F) superexchange interaction between the metal centers having the partially filled d-orbitals. Here, the metal d-orbitals are interacting with the orthogonal ligand orbitals.
(b) 180° superexchange leading to an AF-interaction: A strong antiferromagnetic (AF) superexchange interaction occurs when the partially filled d-orbitals of the metal centers interact at 180° bond angle (i.e., magnetic ion-bridging ligand atom-magnetic ion angle=180°).
(c) GKA rule in terms of overlapping integral: Orthogonal and non-orthogonal integrals: If two orbitals are orthogonal then the overlap integral is zero. It leads to a ferromagnetic exchange when the ligand and the metal orbitals are orthogonal, e.g., d_{xz} and p_z orbital; d_{xy} and p_x orbital; $d_{x^2-y^2}$ and p_y orbital. If two orbitals are non-orthogonal and they can produce a reasonably high overlap integral then it leads to an electron transfer or a partial covalence. This leads to an antiferromagnetic exchange. It happens so when the ligand and metal orbitals are non-orthogonal. For instance, d_{z^2} and p_z; $d_{x^2-y^2}$ and p_x; d_{xy} and p_y orbital.

Rough

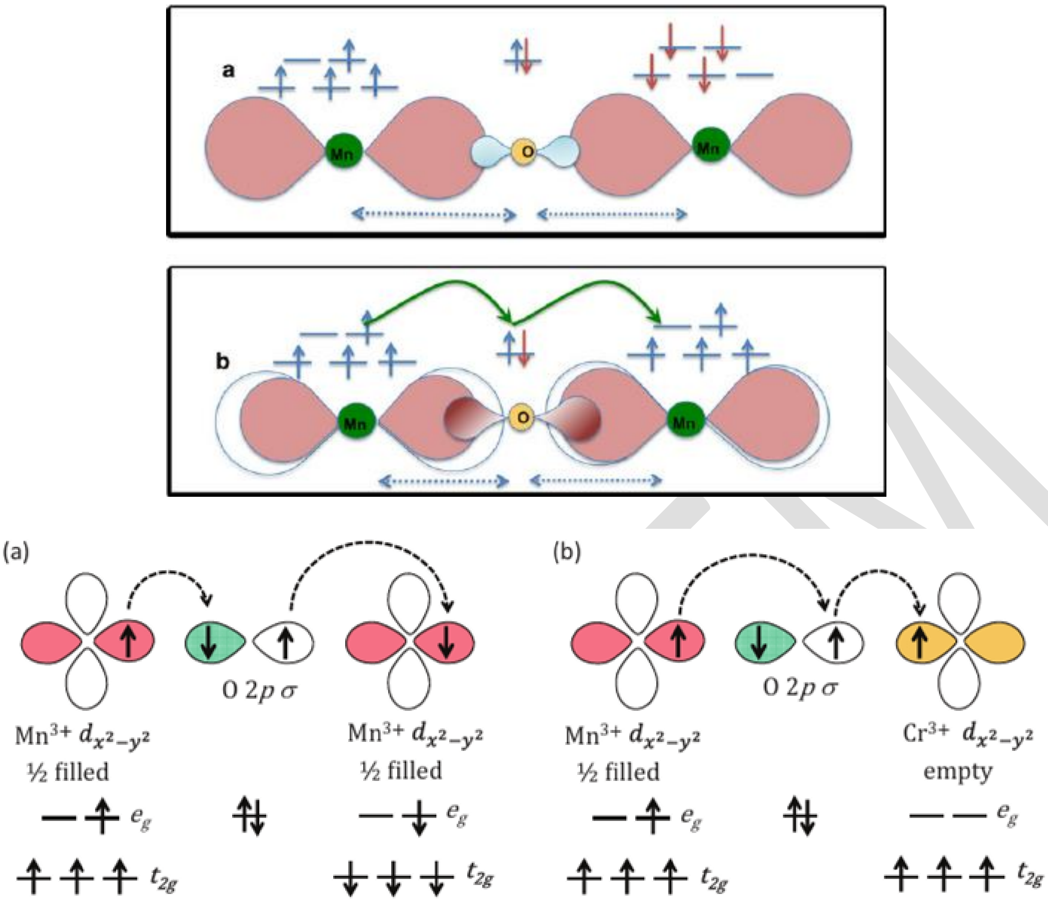


Figure 6: Superexchange in a linear M-O-M system. An example of superexchange via (a) σ-bonding (b) π-bonding

Magnetochemistry- Part V

Magnetic properties of Transition metal ions

The first transition group elements possess an incomplete inner 3d shell. But for these elements the incomplete shell is not effectively shielded from external influence. These 3d orbitals are greatly affected by the ligands such that the rotations of electrons about the nucleus, which are essential for generating the orbital magnetic moment, get significantly restricted (i.e. L becomes zero). This leads to great difficulty in estimating the degree of quenching of the orbital contribution to the magnetic moment, but in some cases the results are easier to interpret than are those for the rare earths.

The ions of the first transition series starting from scandium, Sc^{3+}, ion and ending with zinc, Zn^{2+}, ion have progressively 0 to 10 electrons in the 3d shell. The first and last members are diamagnetic but all the others with intermediate number of electrons are paramagnetic. It might be supposed that these ions would be alternately paramagnetic and diamagnetic depending on whether they have an odd or an even number of electrons. But, as for the rare earths are concerned, the ions are all paramagnetic because the electrons in the incomplete shell tend not to pair off until these are forced to do so. For instance, in the 3d shell there are 5 orbitals which can accommodate 10 electrons. If 6 electrons are present, they will take 1 paired and 4 unpaired place instead of 3 pairs. The 4 unpaired electrons will contribute to the paramagnetism. It is therefore an easy matter to compute the number of unpaired electron spins in any given ion. The difficulty that arises is in connection with the orbital contribution. The orbital moments of these ions are not free to move as they are for the rare earths, and yet, on the other hand, they may not be entirely quenched. But the best agreement with the experiment is obtained by completely neglecting the orbital motion. For all the transition metal ions the magnetic moments are calculated by using following equations

$$\mu_J = \sqrt{J(J+1)}\, g\beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}\, \beta \ldots\ldots\ldots\ldots\ldots (2)$$

For spin only magnetic moment, L= 0, so that J = S and hence g=2. Therefore

$$\mu_S = \sqrt{4S(S+1)}\, \beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

$$\mu_S = \sqrt{n(n+2)}\, \beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where n = number of unpaired electrons

Let us calculate μ_J, μ_{L+S} and μ_S for one transition metal ion using equation (1), (2) and (3). For example, Cr^{3+} has d^3 configuration, thus,

l	2	1	0	-1	-2
	↑	↑	↑		

Total spin quantum number (S) = 1/2 + 1/2+ 1/2 = 3/2

Spin multiplicity (2S+1) = 4

Total angular momentum number (L) = (2×1) + (1×1) + (0×1) = 3

J = L+S, L+S-1,……L-S. i.e., J = 9/2 to 3/2. According to Hund's rule J =3/2 is chosen for the calculation of g,

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$$g = \frac{3}{2} + \frac{3/2(3/2+1) - 3(3+1)}{2 \times 3/2(3/2+1)}$$

$$g = \frac{3}{2} + \frac{15 - 48}{30} = 0.4$$

Calculation of μ_J

$$\mu_J = \sqrt{J(J+1)}\, g\ B.M.$$

$$\mu_J = 0.4\sqrt{3/2(3/2+1)}\ B.M.$$

$$\mu_J = 0.8\sqrt{15/4}\ B.M$$

$$\mu_J = 0.77\ B.M$$

Calculation of μ_{L+S}

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}\ B.M.$$

$$\mu_{L+S} = \sqrt{4 \times \frac{3}{2}\left(\frac{3}{2}+1\right) + 3(3+1)\ B.M.}$$

$$\mu_{L+S} = \sqrt{\left(4 \times \frac{3}{2} \times \frac{5}{2}\right) + (3 \times 4)\ B.M}$$

$$\mu_{L+S} = \sqrt{27}\ B.M = 5.20\ B.M.$$

Calculation of μ_S

$$\mu_S = \sqrt{n(n+2)}\ B.M.$$

$$\mu_S = \sqrt{3(3+2)}\ B.M. = 3.87\ B.M.$$

$$\mu_S = 3.87\ B.M.$$

Observed μ_{eff} for the Cr^{3+} is 3.68 – 3.86 B.M., very close to spin only magnetic moment μS. Similarly, μ_J, μ_{L+S} and μ_S can be calculated for the other transition metal ions.

Table 1: Magnetic properties of first transition series metal ions

d^n	Ion	S	L	Ground term	μ_J	μ_{L+S}	μ_S	μ_{exp}
d^0	Sc^{3+} Ti^{4+} V^{5+}	0	0	$^1S_0$	0	0	0	0
d^1	Ti^{3+} V^{4+}	½	2	$^2D_{3/2}$	1.55	3.00	1.73	1.7-1.8
d^2	Ti^{2+} V^{3+}	1	3	$^3F_2$	1.63	4.47	2.83	2.7-2.9
d^3	V^{2+} Cr^{3+} Mn^{4+}	3/2	3	$^4F_{3/2}$	0.77	5.20	3.87	3.7-3.8
d^4	Cr^{2+} Mn^{3+}	2	2	$^5D_0$	0	5.48	4.90	4.9-5.3

d^5	Mn^{2+} Fe^{3+}	5/2	0	$^6S_{5/2}$	5.92	5.92	5.92	5.9
d^6	Fe^{2+} Co^{3+}	2	2	$^5D_4$	6.70	5.48	4.90	5.1-5.5
d^7	Co^{2+}	3/2	3	$^4F_{9/2}$	6.64	5.20	3.87	4.3-5.2
d^8	Ni^{2+}	1	3	$^3F_4$	5.59	4.47	2.83	2.8-4.0
d^9	Cu^{2+}	½	2	$^2D_{5/2}$	3.55	3.00	1.73	1.7-2.2
d^{10}	Cu^{+} Zn^{2+}	0	0	$^1S_0$	0	0	0	0

The magnetic moments, both theoretical and experimental, of the first transition series metal ions are shown in Table 1. Referring to the table, the magnetic moments obtained using μ_J equation are different from that obtained from μ_S equation. Besides, the magnetic moments obtained using μ_{L+S} equation are also different those of μ_S equation in most cases. For most metal ions in the table, L= 0 and μ_{L+S} equation reduces to μ_S equation. Thus, magnetic moments of most first transition series metal ions are given by μ_S equation. However, the magnetic moments of Co(II) and Ni(II) worked out experimentally are considerably higher than those expected from μ_S equation. The experimental magnetic moment (μ_{exp}) shown in the given table represents both tetrahedral and octahedral complexes.

A plot of the observed magnetic moments of the ions with the d^0 to d^{10} configurations against d^n gives a single humped curve passing through a maximum at d^5 (HS)

Magnetic Properties of Coordination Complexes: Crystal Field Theory

The magnetic behaviour of coordination complexes can be easily explained using crystal field theory. In general, the ligands having very high splitting energy leads to the formation of low spin complexes, since the gap between t_{2g} and e_g level is much higher. However, for low field ligands splitting are less and thus they lead to the formation of high spin complexes.

Consider the complex $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$, in both the cases (Fig. 1), Fe is in the (+2) oxidation state and has octahedral geometry but the complex with CN- as ligand forms a low spin diamagnetic complex (where all the electrons are paired up) whereas the complex with H_2O as the ligand form high spin complex. This can be explained based on different ligand coordination taking place with the same metal ion that is CN- and H2O in this case. CN- is a strong field ligand that leads to high amount of crystal field splitting and thus forms low spin complexes whereas H_2O is a weak field ligand which give rise to lower splitting and thus forms high spin paramagnetic complexes. This difference is explained with the help of following figure.

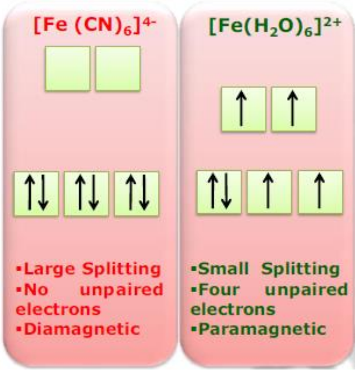


Fig. 1

Hence, the ligands lying at the end of the spectrochemical series are high field strong ligands which form low spin complexes. Examples include ethylenediamine (en), NO_2^-, CN^-, CO etc. As we have already discussed that the magnetic moment, μ, for the complexes of 3d metal ions, can be deduced from spin only formula (Equation 4). This formula works reasonably well with the metal ion of the first transition series. In case of the metals of second and third transition series, equation 4 is not applicable. For 4d and 5d metal ion the angular orbital moment along with the spin motion makes a large contribution. Since the complex $[Fe(CN)_6]^{4-}$ is diamagnetic in nature thus, its magnetic moment is zero, but for the complex$[Fe(H_2O)_6]^{2+}$ it can be calculated as follows;

For $[Fe(H_2O)_6]^{2+}$, n = 4; $\mu s = [\ 4(4+2)\ ]^{1/2} = 4.90$ BM

Observed μ_{eff} for the high spin complexes of Fe^{2+} is 5.10 – 5.70 B.M., very close to spin only magnetic moment μ_S. The calculated and experimental magnetic moments for complexes of 3d transition metal ions are given in Table 2.

Table 2:

d^n	Ion	n	HS		n	LS	
			μ_{obs}	μ_{cal}		μ_{obs}	μ_{cal}
d^1	Ti^{3+}	1	1.73	1.73	-	-	-
d^2	V^{3+}	2	2.7-2.9	2.83	-	-	-
d^3	Cr^{3+}	3	3.7-3.9	3.87	-	-	-
d^4	Cr^{2+}	4	4.75-4.9	4.90	2	3.2-3.3	2.83
d^5	Mn^{2+} Fe^{3+}	5	5.65-6.1 5.7-6.0	5.92 5.92	1	1.8-2.1 2.0-2.5	1.73
d^6	Fe^{2+}	4	5.1-5.7	4.90	0	-	-
d^7	Co^{2+}	3	4.3-5.2	3.88	1	1.8	1.73
d^8	Ni^{2+}	2	2.8-3.5	2.83	-	-	-
d^9	Cu^{2+}	1	1.7-2.2	1.73	-	-	-

Spin-Orbit Coupling

As already pointed out that some of the first transition series metal complexes (e.g., low spin Fe^{3+}, high spin Fe^{2+}, and Co^{2+}) give magnetic moment much higher than calculated from the μ_s equation. So, every metal ion except for d^1, d^2, low spin d^5 and high spin d^6 and d^7 follow spin only formula. The valance bond theory does not offer any explanation for this higher magnetic moment, but the crystal field theory does.

As we know that classical model of orbital magnetic moment assumes that the electrons must go around the nucleus so that Amperes theorem is applicable. In most of the transition metal complexes the motion of electrons is very much restricted, so that effectively orbital magnetic moments quenched.

The unpaired electrons in a first transition series metal ion are in the 3d orbitals. A transition metal ion has five degenerate 3d orbitals. For these electrons to the orbital magnetic moment, the electrons should go around the nucleus via these orbitals. In such a case spin-orbit coupling takes place and contributes to the overall moment (i.e. $\mu_{eff} > \mu_s$). Spin-orbit coupling is the interaction of an electron's orbital angular momentum and its spin angular momentum leading to a magnetic moment. For spin-orbit coupling to occur, the following three conditions must be satisfied:

1. There must be a half-filled or empty orbital similar in energy to the orbital holding the unpaired electron(s).
2. There must be a half-filled or empty orbital similar in shape and symmetry, i.e., they should be transformable into one another by rotation about same axis.
3. The nearby symmetry related orbital must not contain an electron with the same spin as the first one (Hund`s rule).

Electron in this orbital can make use of this nearby orbital vacancy (by moving into it) to circulate around the center of the complex and generate orbital momentum (μ_L). This leads to additional magnetic moment. As we know that spin-orbit coupling means that S and L do not operate independently and J states need to be defined. But spin-orbit coupling is usually small for lighter transition metals; we can treat S and L independently (as was done in the earlier equation for μ_{L+S}). This is not true for heavy metals and their magnetism is much more complicated to predict.

Orbital Contribution to the Magnetic Moment in Transition Metal Ions

Orbital Contribution from e_g Orbital Set

For orbital angular momentum to contribute, and hence for the paramagnetism to differ significantly from the spin-only value, the orbital in which electron resides must be able to transform the orbital it occupies into an equivalent and degenerate orbital by a simple rotation (it is the rotation of the electrons which induces the orbital contribution). In a free ion, the five d-orbitals are degenerate and some orbitals can be transformed into others by rotations. A 90° or 45° rotation about z-axis transform dxz↔dyz, dxy↔dyz, dxy↔dxz and dxy↔dx^2-y^2 orbitals (Fig. 2), respectively. In an octahedral complex, due to crystal field splitting, the five d orbitals split into two sets of orbitals of different energy (t_{2g}: dxy, dxz, dyz and e_g: dx^2-y^2, dz2). The energy barrier between these two sets restricts the orbital magnetic moment of the electrons. The degeneracy between the dxy and dx^2-y^2 orbitals is also removed, the transformation dxy↔dx^2-y^2 is now restricted. In an octahedral field, dx^2-y^2 and dz^2 orbitals are degenerate, but the shapes of these orbitals are such that one is not transformable into the other by rotation. Thus, due to the condition 2 discussed in previous section the eg orbital set-in octahedral geometry (e orbital set-in tetrahedral geometry) cannot generate any orbital magnetic moment. Hence, the, dx^2-y^2 and dz^2 orbitals (e_g orbital set) are known as nonmagnetic doublet. These orbitals are nonmagnetic in the sense of orbital magnetic moment; however, spin magnetic moment is still generated by these orbitals.

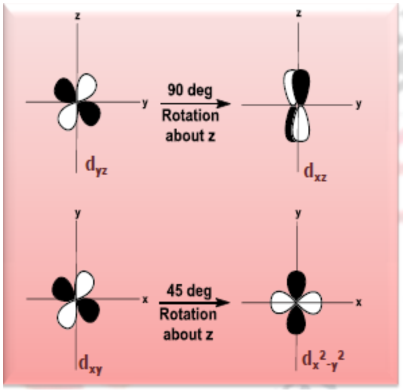
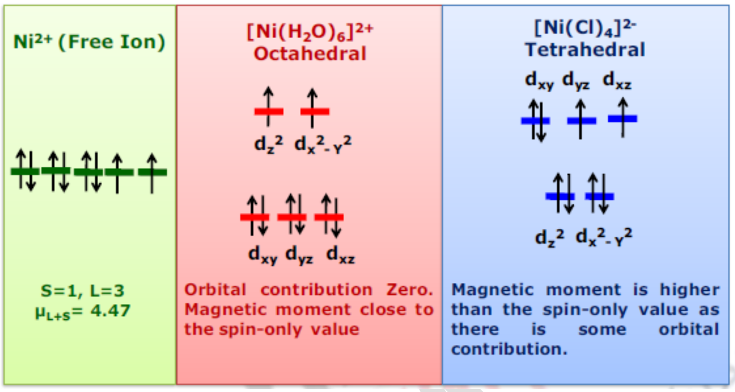


Fig. 2



Orbital contribution Zero. Magnetic moment close to the spin-only value

Magnetic moment is higher than the spin-only value as there is some orbital contribution.

Fig. 3

Orbital Contribution from t_{2g} Orbital Set

The t_{2g} set of orbitals dxy, dxz and dyz are similar in energy, shape and symmetry. For example, the dxy and dyz orbitals are degenerate; moreover, the dxy orbital can transformed into dyz orbital by rotating it through 90° about the z-axis. There is a further factor that needs to be taken into consideration: if all the t_{2g} orbitals are singly occupied, an electron in, say, dxy orbital cannot be transferred into dyz orbital because it already contains an electron having the same spin quantum number as the incoming electron; if all the t_{2g} orbitals are doubly occupied the transfer is not possible. Thus, only configurations which have t_{2g} electron other than three or six electrons make orbital contributions to the magnetic moments for octahedral complexes. Thus, octahedral complexes with d^1 and d^2 configurations will have orbital magnetic moment but the octahedral complexes with d^3 configuration will have no such moment. The expected orbital contribution in high-spin octahedral or tetrahedral complex with any of the d^1 to d^{10} complexes is shown in Table 3

This table also lists the ground state terms corresponding to the d^n configurations. When an electron distribution can take up only one arrangement, the corresponding ground state term is singlet (A); when two arrangements are possible, ground state term is doublet (E) and for three arrangements, ground state term is triplet (T). In a term symbol, the left-hand superscript denotes the spin multiplicity and the right-hand subscript g indicates gerade (a tetrahedron has no inversion centre and hence the subscript g is not used for tetrahedral complexes). Looking at the table, metal ions having A and E ground state terms do not show orbital contributions, however, those having T ground state terms are expected to show orbital contributions to the effective magnetic moment. This explains why the effective magnetic moment for tetrahedral Ni^{2+}, octahedral Co^{2+}, and octahedral Fe^{2+} complexes are higher than the spin–only value.

An example helps to understand the quenching of orbital moment in different metal complexes. Let us consider $Ni^{2+}(d^8)$ complex. As a free ion, the total magnetic moment μ_{L+S} is calculated to be 4.47. In octahedral d^8 complex, the orbital contribution is zero. On the contrary, d8 tetrahedral complex will have contributions from the orbital magnetic moment. Hence, although both the complexes have two unpaired electrons, the $[Ni(H_2O)_6]^{2+}$ has magnetic moment close to the spin-only value, but the magnetic moment in $[NiCl_4]^{2-}$ is higher than the spin-only value (Fig. 3).

Orbital Contribution from Excited States

From above discussion the octahedral Ni^{2+} or tetrahedral Co^{2+} are expected to have no orbital magnetic moment, but only spin magnetic moment. However, such a complex exhibit (in reality) a magnetic moment significantly higher than μ_S. This is because the excited states of octahedral Ni^{2+} ($t_{2g}^5e_g^3$, $^3T_{2g}$) and tetrahedral Co^{2+} ($e^3t_2^4$, $^4T_2$) carry the orbital magnetic moment. In a system having such an excited state, the spin-orbit coupling brings about some mixing of the ground state with the excited state, thus forcing some orbital contribution. The quantitative relation between μ_{eff} and μ_S is

$$\mu_{eff} = \mu_s\left[1 - \frac{\alpha\lambda}{\Delta}\right] + \frac{2\alpha N\beta^2}{\Delta} \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where α is a constant which depends upon the ground state and the number of d electrons. The value of α is 2 for E_g ground state term and 4 for an A_{2g}. Δ is the separation between ground and the excited state and can be obtained from the electronic spectra. λ is the spin-orbit coupling constant and it is positive for d^1, d^2, d^3 and d^4 ions and negative for d^6, d^7, d^8 and d^9 ions. The first term $\alpha\beta^2/\Delta$ arises from the mixing in of an excited state via spin-orbit coupling and the second term $2\alpha N\beta^2/\Delta$ is the temperature independent paramagnetism which is field induced. Now it is clear from the above relation that the greater the 10Dq value, the smaller the mixing effect, therefore, the lesser orbital contribution. i.e., a strong donor ligand is likely to reduce the orbital contribution. Further, depending upon the sign of λ, μ_{eff} will be higher or lower than μ_S. For example, the sign of λ is negative for Ni^{2+} (d^8) and positive for Cr^{3+} (d^3).

The high spin octahedral complex of Mn^{2+} (d^5), $[Mn(H_2O)_6]^{2+}$ with the ground state $^6A_{1g}$, has no excited state of same spin multiplicity as that of the ground state. Therefore, mixing of the ground state with any of the excited states due to spin-orbit coupling is not possible. Thus, there is no orbital contribution to μ_{eff} due to spin-orbit coupling. Therefore, μ_{eff} is same as μ_S. In high spin octahedral complexes of Co^{2+} (d^7), the ground state is $^4T_{1g}$ and a large orbital contribution to the magnetic moment is expected. Mixing of excited state lowers the moment somewhat, but a value of μ_{eff} (4.30–5.20) is still larger than the μ_S (3.88) more than 5 B.M. is usually found. The ground state for the tetrahedral complexes of Co^{2+} (d^7), is $^4A_2$ and a low magnetic moment approaching to spin only value might be expected. However, an excited magnetic state is comparatively low in energy in the tetrahedral complexes and can be mixed with the ground state. So, the magnetic moments in the range from 4 to 5 B.M. have been predicted and are found experimentally. An inverse relationship exists for tetrahedral complexes between the magnitude of the moment of the complex and the value of Δ as predicted by equation (5).

In general, using three conditions discussed in the previous section, it is also possible to make out whether a low spin octahedral configuration will have orbital contribution or not. For example, in a low spin complex of Mn^{2+} (d^5), the ground state is $^2T_{2g}$ and therefore fulfils all the three conditions. So, the complex will have orbital contribution. The ground state for low spin complex of Fe^{2+} (d^6) ion is A_{1g} but all the electrons are paired and hence the complex is diamagnetic. Moreover, the ground state for low spin complex of Co^{2+} (d^6) ion is ^2Eg and hence it has no orbital contribution.

For the 4d and 5d ions, diamagnetism results for even numbered electrons, and paramagnetism to the extent of one unpaired electron only is observed for the odd numbered electrons, indicating that spin pairing takes place for these ions as far as possible. This may be due to (i) reduced interelectronic repulsions in large sized ions reducing the electron pairing energies, (ii) higher ligand field splitting. The μ at room temperature is generally lower than μ_S and cannot be used to determine the unpaired electrons due to (iii) high spin-orbit coupling constants which align L and S vectors in opposite directions destroying the paramagnetism. Further, (iv) the Curie or Curie-Weiss law does not hold, the variation of μ with L is complex and depends upon the number of the electrons present.

Some ions like MnO_4^-, CrO_4^{2-} and low spin Co^{3+} complexes show temperature-independent paramagnetism (TIP) even though they do not have any unpaired electron. This is due to the spin-orbit coupling of the ground state to a paramagnetic excited state under the influence of the magnetic field. The degree of mixing is independent of temperature, but depends on the applied magnetic field, as the excited state is well separated from the ground state, whose population does not change with temperature.

Quenching of Orbital Magnetic Moment due to Loss of Orbital Degeneracy

The loss of degeneracy of the d orbitals affects the unrestricted motion of electrons about the nucleus. The degeneracy of d orbitals is lost (Fig. 4) to a greater extent in case of tetragonally distorted octahedral complex, trigonal bipyramidal complex and square pyramidal complex. In such a complex, the magnetic moment μ_{eff} is close to μ_S.

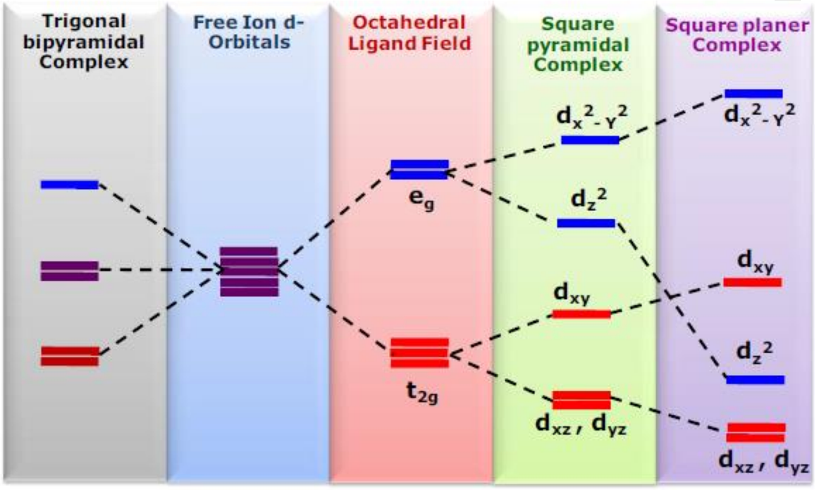


Fig. 4

Magnetic properties of lanthanides

The lanthanides (La to Lu) are generally trivalent, belong to the inner transition series. +3 oxidation is the most common oxidation states of lanthanides (+2, +4 are also possible). Lanthanides have valence shell electronic configuration of $4f^{0-14}5s^2 5p^6$. The magnetic moment (paramagnetism) in them arises from electrons of 4f level. Since, the 4f level is incompletely filled and is too far inside (i.e., effectively shielded by the filled 5s and 5p subshells) to be influenced by the surrounding coordinating ligands, a trivalent lanthanide complex serves as a true ion. The 4f electrons are relatively free from external influence is given by the facts that the Lanthanides are remarkably alike chemically, and that their absorption bands and magnetic susceptibilities are little affected by change of ionic environment as by change of compound or of solvent. The crystal field effect in lanthanides is about 1/100 of that observed in the first transition series. This suggests that for lanthanides the spin-orbit coupling constant is quite high (spin-orbit coupling >> ligand field splitting), and thus $\vec{L}$ vector and $\vec{S}$ vector couple effectively to give $\vec{J}$ vector. For lanthanides, J is a good quantum number. This is simply equivalent to assuming the multiplet all very wide compared to kT. The magnetic moment (μ_J) will be given by the following equation

$$\mu_J = \sqrt{J(J+1)}\, g\beta$$

Where

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)}$$

On simplifying this equation we get

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

Where; J = L+S, L+S-1,……L-S.

For the calculation of g value, we use minimum value of J for the configurations having up to half-filled f orbitals; i.e. J = L−S for f^0-f^7 configurations. And maximum value of J is used for configuration with more than half-filled f orbitals; i.e. J = L+S for f^8-f^{14} configurations. For f^0 (La), f^7 (Gd), and f^{14} (Lu), L = 0, hence μ_J automatically reduces to μ_S.

Now let us calculate Landè factor g and μ_J for a Pr^{3+} ion. Pr^{3+} has electronic configuration - $[Xe]4f^2$.

Ground State from Hund's Rules is shown in figure 2

l	3	2	1	0	-1	-2	-3
	↑	↑					

Thus, total spin quantum number (S) = 1/2 + 1/2 = 1

Spin multiplicity (2S+1) = 3

Total angular momentum number (L) = 3 + 2 = 5

J = 6, 5, 4. ^3H state splits into $^3H_4$, $^3H_5$ and $^3H_6$ states. According to Hund's rule 3H4 is the ground state and energies of these states increase in the order $^3H_4 < {}^3H_5 < {}^3H_6$. Thus, J =4 is chosen for f^2

$$g = \frac{3}{2} + \frac{1(1+1) - 5(5+1)}{2 \times 4(4+1)}$$

$$g = \frac{3}{2} + \frac{2 - 30}{40} = 0.8$$

$$\mu_J = 0.8\sqrt{4(4+1)}\, B.M$$
$$\mu_J = 0.8\sqrt{20}\, B.M$$
$$\mu_J = 3.58\, B.M$$

This calculated value is very close to the experimental value μ_J = 3.4 - 3.6 B.M.

Similarly, we can calculate Landè factor g and μ_J for all the lanthanide (III) ions. The calculated and observed magnetic moment for the trivalent lanthanides are given in the Table 4

Table 4: Magnetic properties of trivalent lanthanides

Ln	Ln (III) ion	Unpaired electrons	Term symbol	G	μ-calculated	μ-observed
Ln	$4f^0$	0 (L = 0, S = 0)	$^1S_0$	1	0	Diamagnetic
Ce	$4f^1$	1 (L = 3, S = 1/2)	$^2F_{5/2}$	6/7	2.54	2.3-2.5
Pr	$4f^2$	2 (L = 5, S = 1)	$^3H_4$	4/5	3.58	3.4-3.6

Nd	$4f^3$	3 (L = 6, S = 3/2)	$^4I_{9/2}$	8/11	3.62	3.5-3.6
Pm	$4f^4$	4 (L = 6, S = 2)	$^5I_4$	3/5	2.68	-
Sm	$4f^5$	5 (L = 5, S = 5/2)	$^6H_{5/2}$	2/7	0.84	1.5-1.6
Eu	$4f^6$	6 (L = 3, S = 3)	$^7F_0$	1	0	3.4-3.6
Gd	$4f^7$	7 (L = 0, S = 7/2)	$^8S_{7/2}$	2	7.94	7.8-8.0
Tb	$4f^8$	6 (L = 3, S = 3)	$^7F_6$	3/2	9.72	9.4-9.6
Dy	$4f^9$	5 (L = 5, S = 5/2)	$^6H_{15/2}$	4/3	10.63	10.4-10.5
Ho	$4f^{10}$	4 (L = 6, S = 2)	$^5I_8$	5/4	10.60	10.3-10.5
Er	$4f^{11}$	3 (L = 6, S = 3/2)	$^4I_{15/2}$	6/5	9.57	9.4-9.6
Tm	$4f^{12}$	2 (L = 5, S = 1)	$^3H_6$	7/6	7.63	7.1-7.4
Yb	$4f^{13}$	1 (L = 3, S = 1/2)	$^2F_{7/2}$	8/7	4.54	4.4-4.9
Lu	$4f^{14}$	0 (L = 0, S = 0)	$^1S_0$	1	0	Diamagnetic

Landé formula fits well with observed magnetic moments for all the lanthanides except Sm^{3+} and Eu^{3+}. The magnetism of these two ions is best studied in combination with that of promethium (III) and terbium (III). The magnetic behavior of all of these can be explained from the energy separation between ground state and first excited state (in terms of spin orbit coupling constant, λ). The J values for these four ions are shown in Fig. 5. The energy separation between the ground state and the first excited state for Pm (III), Tb (III), Sm (III) and Eu (III) are 5λ, 6λ, $7/2\lambda$ and λ respectively. λ is the spin-orbit coupling constant, and is about 1000 cm^{-1} for all the lanthanides except Sm^{3+} and Eu^{3+}. However, the same for Eu (III), $\lambda \sim 230$ cm^{-1} (very close to kT, 200 cm^{-1} at RT), and for Sm (III) = 840 cm^{-1} (which is also a small value). The magnitude of separation between the adjacent states of a term indicates the strength of the spin-orbit coupling, and in all cases, except Sm^{3+} and Eu^{3+}, it is sufficient to render the first excited state of the Ln^{+3} thermally inaccessible, and so the magnetic properties are determined only by their ground state. Therefore, at room temperature, the first excited state of Sm (III) and first, second and third excited state of Eu (III) are populated. In each of these ions, the J value of an excited state is higher than that of ground state and μ values are expected to be higher than that of calculate one. However, the energy separation in Pm (III) and Tb (III) is large enough and the obtained results from μ_J equation and experimental method are exceedingly close to each other. The magnetism of these ions is expressed by equation (17).

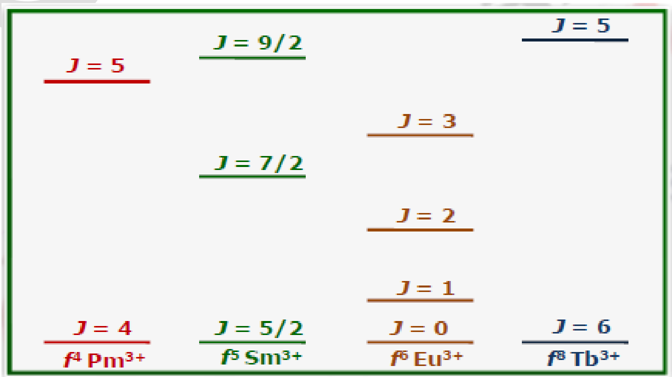


Fig. 5

Theoretical effective Bohr magneton numbers calculated from the appropriate equations of Van Vleck are in extraordinarily good agreement with observed values. In Fig. 6, the plot of variation of magnetic moment (calculated) of lanthanide is a double humped curve and is shown below

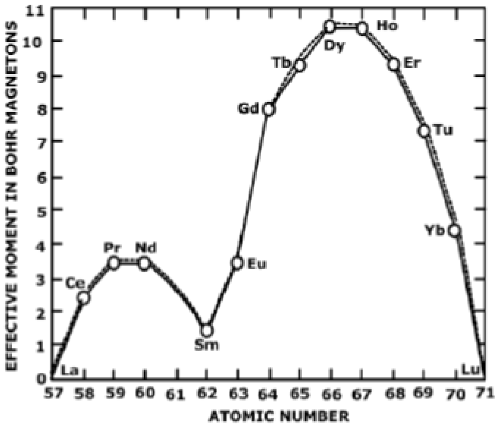


Fig. 6

As the 4f electrons are not involved in chemical bonding, the spin-spin interchange through superexchange to be insignificant in the lanthanides. The high coordination number of a lanthanide complex also mitigates the superexchange interaction. The magnetic exchange phenomenon occurs predominantly through the dipole-dipole interaction in a lanthanide complex.

Note:

(a) Lanthanoid ions other than f^0 (La^{3+} and Ce^{3+}) and f^{14} configurations (Yb^{2+} and Lu^{3+}) are paramagnetic.

(b) Magnetic moment (μ) originates from both spin and orbital contributions.

(c) Spin-orbit coupling is quite large (orbital angular momentum contributes) and only ground state is populated. Magnetic moment of Ln (III) ion is given by $\mu = g[J(J+1)]^{1/2}$

(d) Ligand field effects are small because the 4f orbitals do not effectively interact with the ligands (no quenching because f orbitals are too deep inside).

(e) For Sm^{3+} and Eu^{3+}, spin-orbit coupling is not large enough to prevent occupation of the first excited state at room temperature (thermal energy overcomes the barrier). Mixing of these states with higher J values causes observed magnetic moments to be higher.

Use of Lanthanides Magnetic Moment

1. NMR Shift Reagents - paramagnetism of lanthanide ions is utilized to spread resonances in 1H NMR of organic molecules that coordinate to lanthanides.

2. Lanthanide metals and alloys have interesting ordered magnetism effects. For example, $SmCo_5$ and $Nd_2Fe_{14}B$ show ferromagnetic properties. Thus, they are permanent magnets having following interesting properties;

a) They are light weight.
b) High saturation moments.
c) High coercivity.
d) High magneto crystalline anisotropy.
e) Superior performance magnets for magnetic bearings / couplings / wave tubes.

3. Synthetic rare earth garnets e.g. $Ln_3Fe_5O_{12}$ and $Y_3Fe_5O_{12}$ show interesting ferrimagnetism.

Magnetic properties of actinides

Magnetic properties are more complex than those of lanthanoids. Susceptibility is roughly parallel to the lanthanides but spin orbit coupling is larger than lanthanides and equation used for lanthanoid is not suitable. This is because 5f electrons interact much more with ligands and hence spin orbit coupling and ligand field effects are of comparable magnitude (4f orbitals are effectively shielded by the $5s^2 5p^6$ outer subshells while the 5f electrons are poorly shielded and sometimes left bare, depending on the oxidation state). Thus, actinides are under a much greater crystal filed effects than the lanthanides. Usually, the crystal field effect in an actinide is about one tenth of first transition series metal ions and almost ten times more than lanthanides. The magnetic superexchange is more important in actinides (compared to lanthanides), especially magnetic exchange of complexes of lighter actinides. Experimental paramagnetic moment varies with temperature and lower than lanthanides.

In actinides, j-j coupling is considerable and for same f^n configuration, the experimental magnetic moment of an actinide is somewhat lower than that of a lanthanide. An exposure of the $5f^n$ electrons of an actinide to a crystal field may lead to a considerable quenching of the orbital magnetic moment. As for Sm (III) and Eu (III), so too far for Pu (III) and Am (III), the observed magnetic moment can be explained based on the existence of the thermally controlled population of both ground state and the intermediate excited state (Sm(III) and Pu(III) have f^5 and Eu(III) and Am (III) have f^6 configuration).

Table: Experimental and theoretical magnetic moments

f^n	An-ion	Compound	Term symbol	μ_J	μ_{exp}
1	U(V)	UCl_5	$^2F_{5/2}$	2.54	1.7
	Np(VI)	NpF_6			2.0
2	U(IV)	$[N(Me)_4]_2UCl_6$	$^3H_4$	3.58	2.2
	Pu(VI)	PuF_6			0.6
	Np(V)	$NpO_2(C_2O_4H).2H_2O$			3.2
3	Np(IV)	$KNpF_5$	$^4I_{9/2}$	3.62	2.9
4	Pu(IV)	$[N(Me)_4]_2PuCl_6$	$^5I_4$	2.68	1.8
5	Pu(III)	PuF_3	$^6H_{5/2}$	0.84	1.2
6	Am(III)	AmF_3	$^7F_0$	0	1.6
7	Cm(III)	CmF_3	$^8S_{7/2}$	7.94	7.9