1 Introduction

1.1 Lanthanides

The term “lanthanide” was introduced by Victor Goldschmidt with the name of its first element “lanthanum”.[1] It has the outer electronic configuration $6s^2 5d^1 4f^0$, so it can either be considered as a d-block elements or an f-block element. The relative energy of the 5d and 4f orbitals are very similar and sensitive to occupancy of orbitals but on the basis of stability of 4f shell which is slightly more compare to 5d shell, it was considered as f-block element. This criterion was followed by next 14 elements and electrons enter in the 4f shell until at lutetium.[2] The lanthanides are 15 elements in the periodic table considered as the first f-block elements, starting from lanthanum ($_{59}La$) to lutetium ($_{71}Lu$), which are commonly referred as “rare earth metals” along with scandium and yttrium. They are chemically represented by the symbol “Ln”.

1.1.1 Oxidation states

The most characteristic oxidation of the lanthanides is +3 and the electronic configurations for +3 oxidations states (Ln^{3+}) are represented as $4f^n 5d^0 6s^0$ with strict regularity.[2] Other oxidation states like +2 and +4 also exist but they are not generally stable as by losing or gaining one electron they can revert to +3. Eu(II) and Yb(II) are quite stable as they have half ($4f^7$) and completely filled ($4f^{14}$) subshells respectively. Eu(II), Sm(II) and Yb(II) can be prepared in aqueous solution but they can reduce water easily and are oxidized by oxygen. The lanthanides Nd, Dy, Tm and Ho can also form some compounds in the +2 oxidation state but they are stable in the solid state. The +4 oxidation state is shown by Ce, Pr and Tb but only Ce^{4+} is stable in water.[2]

1.1.2 Lanthanide contraction

In lanthanides due to shape of f-orbitals, shielding of one f-electron by another from the effects of nuclear charge is quite weak. So with increasing atomic number and nuclear charge, the effective nuclear charge experienced by each 4f electrons increases and it is apparent from atomic radii of the lanthanides. The atomic radius or ionic radius decreases from La to Lu with increase in atomic number due to lanthanide contraction.[3] The shrinking of atomic radii for Ln^{3+} is shown in Table 1.1.[4] Lanthanide contraction can also be explained in terms of bond lengths. This phenomena was reported in trinuclear series Ni-Ln-Ni (Ln= La to Tb).[5]

1.1.3 Optical properties

The absorption spectra of Ln^{3+} result from f-f transitions unlike the absorption spectra of transition metal result from d-d transitions.[6] The 4f orbitals are deep within atom, thus broadening effect of ligand vibrations are minimized and the absorption spectra of Ln^{3+} ions are typically very narrow in comparison with the d-d absorption bands of transition metals.[7, 8] The parity of ground state and excited state do not change due to laporte forbidden parity of f-f transitions so the absorption coefficient of lanthanides normally becomes very low. The spectral properties of Ln(III) ions are little influenced by external field generated by counter ions or ligand molecules.[6, 7, 9]

Table 1.1 General Properties of lanthanides.[2,4]

Atomic number	Name (symbol)	Electronic configurations	(M^{3+})	Oxidation states	Atomic radius (Ln^{3+}) Å	Ground state
57	Lanthanum (La)	$5d^{1}6s^{2}$	f^{0}	+3	1.216	$^{1}S_{o}$
58	Cerium (Ce)	$4f^{1}5d^{1}6s^{2}$	f^{1}	+3, +4	1.196	$^{2}F_{5/2}$
59	Praseodymium(Pr)	$4f^{3}6s^{2}$	f^{2}	+3, +4	1.179	$^{3}H_{4}$
60	Neodymium (Nd)	$4f^{4}6s^{2}$	f^{3}	+2,+3, +4	1.163	$^{4}I_{9/2}$
61	Promethium (Pm)	$4f^{5}6s^{2}$	f^{4}	+3	1.144	$^{6}H_{5/2}$
62	Samarium (Sm)	$4f^{6}6s^{2}$	f^{5}	+2,+3	1.132	$^{7}F_{0}$
63	Europium (Eu)	$4f^{7}6s^{2}$	f^{6}	+2,+3	1.120	$^{8}S_{3/2}$
64	Gadolinium (Gd)	$4f^{7}5d^{1}6s^{2}$	f^{7}	+3	1.107	$^{8}S_{3/2}$
65	Terbium (Tb)	$4f^{9}6s^{2}$	f^{8}	+3, +4	1.095	$^{7}F_{6}$
66	Dysprosium (Dy)	$4f^{10}6s^{2}$	f^{9}	+2,+3, +4	1.083	$^{6}H_{15/2}$
67	Holmium (Ho)	$4f^{11}6s^{2}$	f^{10}	+2,+3	1.072	$^{5}I_{8}$
68	Erbium (Er)	$4f^{12}6s^{2}$	f^{11}	+3	1.062	$^{4}I_{15/2}$
69	Thulium (Tm)	$4f^{13}6s^{2}$	f^{12}	+2,+3	1.052	$^{3}H_{6}$
70	Ytterbium (Yb)	$4f^{14}6s^{2}$	f^{13}	+2,+3	1.042	$^{2}F_{7/2}$
71	Lutetium (Lu)	$4f^{14}5d^{1}6s^{2}$	f^{14}	+3	1.032	$^{1}S_{o}$

1.1.4 Luminescence

Luminescence refers to the emission of light from a chemical substance when it is excited photonically, chemically or electrically. In photoluminescence, due to absorption (A) of light, electron is excited from ground state to excited states and it comes back to its ground state by loss of thermal energy and emission of a photon of lower energy. If the thermal loss is rapid and excited electron goes directly to the ground state {singlet (S) to singlet (S)} the process is called fluorescence (F). When the excited electron undergoes intersystem crossing (ISC) to a metstable triplet state and then it returns to ground state causing delay due to interconversion of states {singlet (S) to triplet (T)} then the process is called phosphorescence (P). In lanthanides, when the excitation and emission do not become analogous to fluorescence, then the emission of light is generally mentioned as time-resolved fluorescence.10

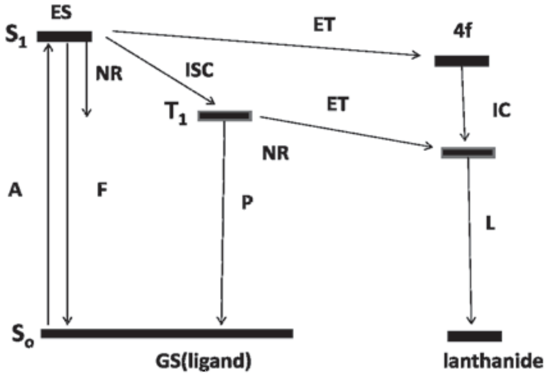

Figure 1.1 Energy diagram showing representation of photoluminescence[6], Abbreviations: L = lanthanide-centered luminescence; ET = energy transfer; IC = internal conversion; GS = ground state, ES = excited state.

Low extinction coefficients dominate the lanthanides luminescence. In general, the lanthanides luminescence[8, 9] is quenched by non-radiative (NR) process. The lanthanides have little luminescence background under ambient conditions; this may be an advantage in applications.[10]

Lanthanides shows very interesting luminescence properties[11] and their two main characteristics are long life times of emission and line-like emission spectrum.[6, 8] In the interest of luminescence, lanthanides have application in luminescent probes,[9] sensors, light amplification,[9] frequency conversion[12-14] and biomedical applications.[15] Anhydrous salts of Ln(III) ions show luminescence and they can be used in solid state laser materials and phosphors for color televisions while the hydrated lanthanides show lower luminescence intensity or no luminescence.[15]

In some applications, water-soluble complexes of Ln(III) are required. One of the drawbacks of lanthanides is that they have high affinity for water molecules, which can quench the excited states.[7] To overcome this problem, it becomes necessary to prevent the water molecules from binding. This can be possible with the help of suitable organic chromophores which can act as an efficient sensitizers for lanthanides.[7] To achieve such behaviour in lanthanide complexes, the ligand must have one or more chromophores and should be able to effectively pass the energy to excited states of Ln(III) ion.[7, 9, 16]

To detect *time-resolved fluorescence*, the lanthanide is sensitized with the help of an organic chromophore and it is called as "antenna" which can act to absorb the excitation light. The absorbed energy is transferred from excited singlet state of antenna to triplet state of Ln(III) ion after that it emits as a photon, this process is shown in Figure 1.2. The energy of triplet state should be little higher than the Ln(III) ion emitting levels, if the energy of triplet state is lower, then reverse transfer (Ln(III) ion to ligand) take place which can reduce the efficiency of sensitized emission.[6, 7]

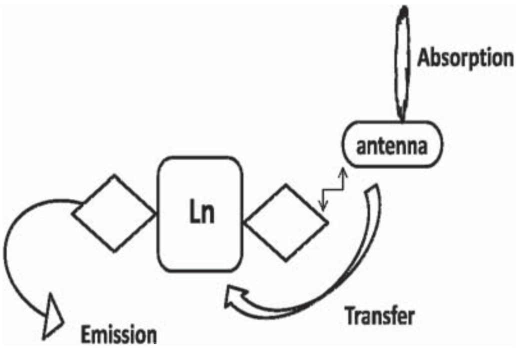

Figure 1.2 Representation of chromophore to acts as an antenna and absorb light which transfer the energy to the lanthanide excited state consequently emitted as a fluorescent signal with a long lifetime.[10]

1.2 Magnetism

Michal Faraday categorised substances either as diamagnetic or paramagnetic. It was followed up to many years, later it has been studied in terms of electronic structure. The origin of magnetism is due to orbital and spin motion of electrons as well as the interaction of these electrons with one another. Some substances have no interaction between the moments of neighbouring atoms, whereas other substances have very strong interactions with the moments of neighbouring atoms. On the basis of these interactions, the magnetic behaviour of substances is divided into six major classes.

1.2.1 Diamagnetism

When a substance is placed in an external magnetic field, there is an induced circulation of electrons producing a net magnetic moment aligned in or against the applied magnetic field. It emerges due to paired electrons of the sample hence it is called diamagnetic effect. These substances do not have net magnetic moments since all the occupied orbital's are containing a pair of electrons. When a substance has all of its electrons paired, this effect dominates and the material is classified as diamagnetic and producing negative magnetization and negative susceptibility. These substances are repelled by magnetic fields. In general, magnetic susceptibility is independent of the temperature and the strength of the applied field.

1.2.2 Paramagnetism

The origin of paramagnetism is due to unpaired electrons in the sample. The spin and orbital motions of electrons gives rise to permanent molecular magnetic moments which align themselves with an applied field. The paramagnetic effect is much stronger in comparison with the diamagnetic effect because it cancels any repulsion between an applied field and paired electrons in the sample. Substances which only have one unpaired electron per molecule also show the net attraction towards magnetic field. In the absence of an externally applied magnetic field, the paramagnetic effect is not observed as the thermal motion in bulk sample has no overall moment (Figure 1.3a). In the presence of applied magnetic field, there is counteraction between the thermal tendency towards randomness and the field capacity to force alignment (Figure 1.3b). As a result paramagnetic effect decreases in magnitude as the temperature is increased. Paramagnetic substances have positive magnetization and positive susceptibility due to partial alignment of the atomic magnetic moments in the direction of the field.

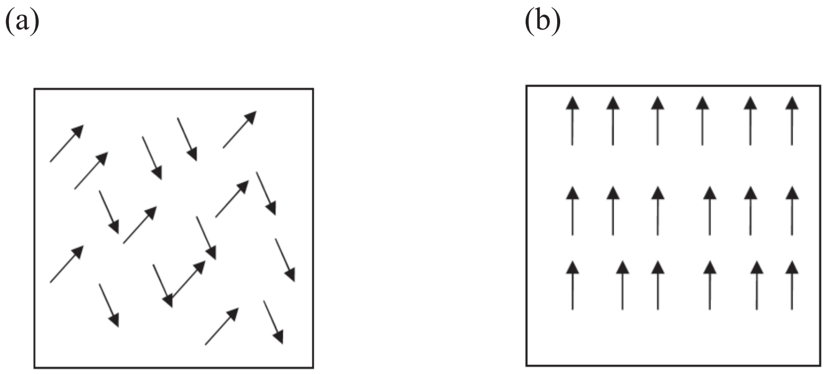

Figure 1.3 (a) In the absence of an external magnetic field electron orientation is random (b) In the presence of an external magnetic field electron oriented in one direction.[2]

The paramagnetic moment originates from spin and orbital motions of unpaired electrons and they have three modes of coupling (spin-spin, orbital-orbital and spin-orbital). In case of the lanthanides, all types of coupling and theoretical paramagnetic moments are considered.[2]

$$\mu = g[j(j+1)]^{1/2}$$

Where j is total angular momentum and g is the Lande splitting factor.

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

So the values of j depend upon total orbital angular momentum quantum number (L) and total spin angular momentum quantum number (S).

Complexes in which the spin-orbit coupling is negligible or nonexistent but they have significant spin and orbital contributions then the theoretical paramagnetic moment, value of μ can be given by,

$$\mu = [4S(S+1) + L(L+1)]^{1/2}$$

It is never completely realized in complexes because the orbital contribution is always less than ideal value. For the first raw transition metal, orbital contribution may be ignored; for the $L = 0$ condition, the value of μ can be given by,

$$\mu = 2[S(S+1)]^{1/2}$$

This is the spin-only formula for magnetic moment. The S will be related to the number of unpaired electrons.

1.2.3 Ferromagnetism

A substance which has interacting magnetic dipoles from its neighbouring paramagnetic centres in such a way that the individual moment is oriented in parallel alignment, then the substance is called ferromagnetic. Parallel alignment leads to an increase in the magnetic moment. In general ferromagnetic substances consist of domains to minimize its free energy. A spontaneous magnetization emerges in each domain even in the absence of a magnetic field. Normally, these substances have very large and positive magnetic susceptibly.[17] Ferromagnetic substances have certain temperature below which magnetic exchange dominates; this temperature value is called the Curie temperature (T_C). Above the Curie temperature, interactions are not strong enough to keep the individual moments in alignment and the substance behaves as a simple paramagnet.

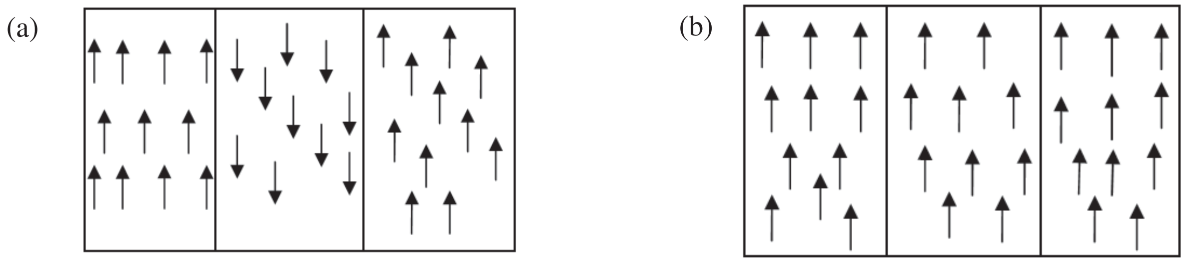

Figure 1.4 (a) In the absence of an external magnetic field the orientation of domains is random. (b) In the presence of an external magnetic field domains oriented in one direction.[2]

1.2.4 Antiferromagnetism

A substance which has interacting magnetic dipoles from its neighbouring paramagnetic centres in such a way that individual moment is oriented in antiparallel alignment then the substance is called antiferromagnetic. Due to complete antiparallel alignment of magnetic moments these substances do not show any spontaneous magnetization. Antiferromagnetic substances have a certain temperature below which magnetic exchange dominates; this temperature value is called the Neel temperature (T_N). Above the Neel temperature, interactions are no longer strong enough to keep the individual moments in alignment analogous to ferromagnetic substances, and they behave as a simple paramagnet.

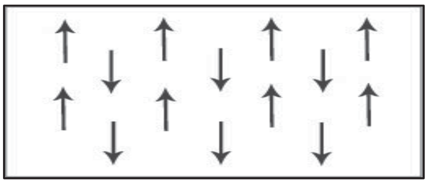

Figure 1.5 In the presence of an external magnetic field orientation of domains.[2]

1.2.5 Ferrimagnetism

In the case of ferrimagnetism,[18] magnetic moments are aligned antiparallel but they have incomplete compensation of the spins. In general, it is due to the unequal number of spins oriented in two directions or two types of spin centres have unequal number of unpaired electrons. Similar to ferromagnets, ferrimagnets also show spontaneous magnetization.

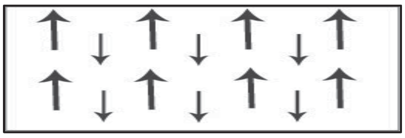

Figure 1.6 In the presence of an external magnetic field orientation of domains.

1.2.6 Canted Antiferrimagnetism

In the case of canted antiferrimagnetism,[19] the equilibrium distribution of moments is not collinear below the Neel temperature. The orientation of spins become canted and due to their incomplete compensation, passes the spontaneous magnetization called as canted antiferromagnetism or weak ferromagnetism.

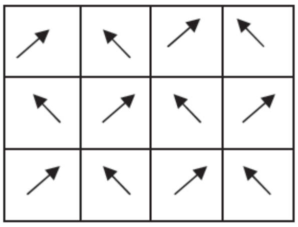

Figure 1.7 In the presence of an external magnetic field orientation of domains.

1.3 Magnetic behaviour

In 1895 Pierre Curie stated that paramagnetic susceptibility is inversely proportional to absolute temperature. This law is known as *Curie's law*.

$$\chi_M = C / T$$

Where χ_M is molar susceptibility, C is the Curie constant and T is the temperature.

The Curie law is fairly applicable for paramagnetic substances, which are magnetically dilute, i.e. the substances, in which paramagnetic centers are well separated from each other by diamagnetic atoms. In materials, which are not magnetically dilute, unpaired spins on neighbouring centers may interact with each other and they do not follow the Curie law. The modified Curie-Weiss law for these substances can be given as below:

$$\chi_M = C / (T - \Theta)$$

Where, Θ is constant with units of temperature.

The magnetic susceptibility v/s temperature can be plotted in three ways. Commonly researchers use the χT versus T to determine the magnetic behaviour of the substances which is as shown in Figure 1.8.

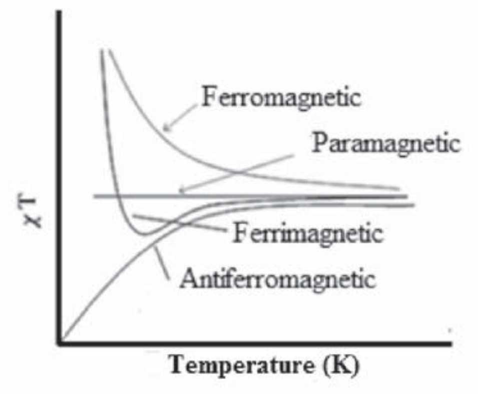

Figure 1.8 Plots of χT *v/s* temperature for paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic materials.

In the case of paramagnetic substances, χT is independent of temperature and a horizontal straight-line is observed in the plot. In the case of antiferromagnets, χT is decreased with lowering in temperature and can be extended to zero (ground state S = 0). In the case of ferromagnets, χT increases as the temperature is decreased, whereas for ferrimagnets, χT first decreases to a minimum and after that it increases abruptly as the temperature is further decreased.

1.4 Single Molecule Magnets (SMM)

It is a class of molecular compounds which shows supermagnetic behaviour below a certain temperature called as the blocking temperate (T_B). These complexes act as nanomagnets, in which every single molecule behaves like an independent magnet. The first time SMM behaviour was observed in manganese cluster (Mn_{12}) of formula $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$, after that in the last two decades many mono and polynulcear complexes have been discovered. SMM have magnetic relaxation many times slower (10^8) than normal molecular paramagnets.[20]

The basic requirement to show SMM behaviour is that the complex should have negative uni-axial magnetic anisotropy (D) and a non zero spin ground state (S). These two parameters combine to give an energy barrier by which slow relaxation of magnetization can take place. This energy barrier for integral spin is calculated by $U_{eff} = |D| S^2$ and for half integral spin $U_{eff} = |D| (S^2 - 1/4)$. The negative uni-axial anisotropy ($D < 0$) removes the degeneracy of ground spin states $(M_S) = \pm S$.

A known example of Mn_{12}-cluster[21-24] has taken to discuss about the SMM. Twelve manganese ions have two types of valencies, four Mn(IV) ions and eight Mn(III) ions are independently coupled with $S = 2$ and $S = 3/2$ respectively. The four Mn(IV) ions are antiferromagnetically coupled with eight Mn (III) ions in the complex so the total spin is $S = 8 \times 2 - 4 \times 3/2 = 10$, therefore $M_S = \pm 10$ (Figure 1.9).

When no external field is applied to the system, energy levels degenerate and probability to find the molecule in either potential well should be equal.[24] In the presence of an applied magnetic field, the degeneracy of energy levels is removed, therefore one potential well preferentially will be more populated in comparison to other.[24] When the applied field is removed then the system will try to come back to thermal equilibrium (relaxation) through the thermally activated energy levels. If the two microstates have equal energy then the probability of quantum tunnelling is increased which is called quantum tunnelling of magnetization.[23, 24]

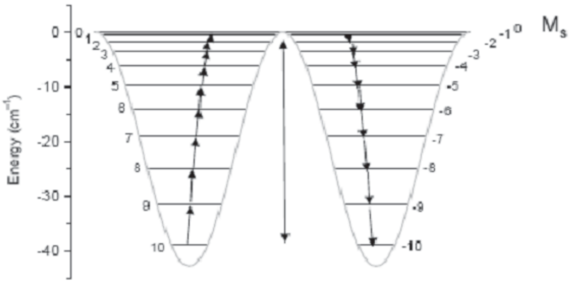

Figure 1.9 Plots of energies of the microstates in S = 10 system.[24]

Magnetisation can be monitored as a function of time. If the energy barrier is high then it is possible to characterise in phase (χ'), out of phase signal (χ'') and hysteresis loops for a molecule. AC-susceptibility measurement of a sample produces two components, one component is susceptibility (χ) and other component is phase shift (ϕ). The phase shift produces a real component of susceptibility and an imaginary component of susceptibility. When real component of susceptibility starts to increase time imaginary component of susceptibility part starts to decrease as shown in Figure 1.10 as a function of frequency and temperature.

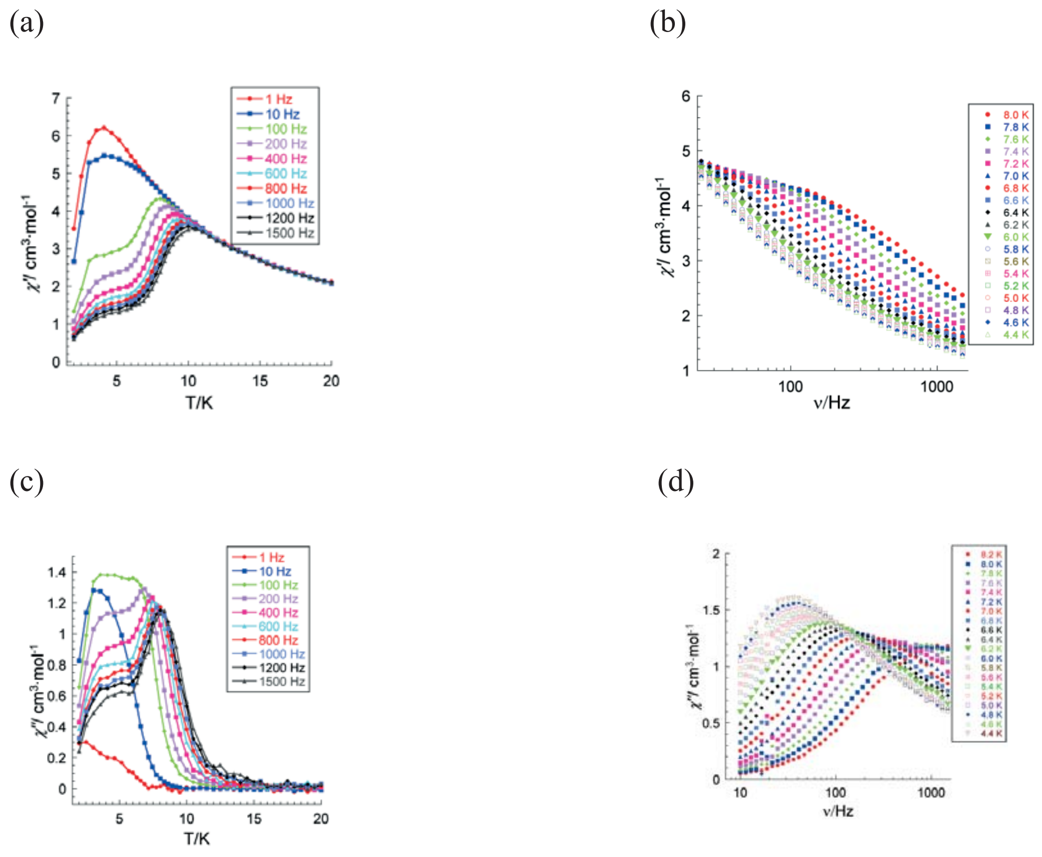

Figure 1.10 AC susceptibility measurements as a function of temperature at different frequencies, and as a function of frequency at different temperatures in-phase (a, b) and out-of-phase signals (c, d).

While the energy levels are thermally activated, energy barrier (U_{eff}) and the relaxation time (τ) can be calculated with the help of Arrhenius expression,

$$\tau = \tau_0 . e^{\left(\frac{Ueff}{K_B T}\right)}$$

If the energy barrier is small enough then the frequency of spin reorientation will be faster and maxima is not observed in out of phase signal or may be no out of phase signal (χ'') is perceived.