



1 Introduction

1.1 Molecular magnetism

Since magnetism had been first discovered by ancient Greeks,^[1] magnets have played a critical role in the history of science and technology.^[2] With the development of science over the centuries applications of magnets have seen a huge expansion, from magneto-mechanical machines to electrical motors and generators, information/telecommunications devices and so on.^[3] Conventional magnets are comprised of transition or rare earth metals or their ions, in which the unpaired electron spins reside in *d*- or *f*-orbitals, and prepared by high-temperature metallurgy. In the past few decades, a new class of molecule-based magnetic materials has been prepared by low-temperature organic chemistry methodologies, comprised of molecular-based species, exhibiting exciting magnetic properties.^[3]

The first organic-based ferromagnet was reported in 1987.^[4] This ionic, zero-dimensional (0-D), polar organic solvent soluble $[\text{Fe}(\text{C}_5\text{Me}_5)_2]^+[\text{TCNE}]^-$ (TCNE = tetracyanoethylene) compound with a critical (Curie) temperature T_c of 4.8 K exhibits magnetic hysteresis and has a saturation magnetization characteristic of a ferromagnet.^[5] Since the discovery of the first molecule-based magnet, a large number of organic- and molecule-based magnets including organic, organometallic or inorganic coordination compounds have been synthesized and characterized.^[6]

In the early 1990s, a coordination complex with formula $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$ was discovered, exhibiting a magnetic hysteresis below a certain blocking temperature T_B .^[7] This behavior resulted from the slow relaxation of magnetization in discrete molecules, thus this class of molecules has been termed single-molecule magnets (SMMs). Since this discovery suggests the possibility of employing molecules as the smallest units for storing magnetic information, a large number of compounds displaying this behavior have been synthesized and reported over the last 20 years.^[8]



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1.2 Magnetic phenomena

The spins associated the unpaired electrons and their interactions with each other determine the magnetic behavior of magnets. Magnetic behavior can be quantified through molar magnetic susceptibility χ . Within a homogeneous magnetic field H , a sample containing 1 mole of molecules acquires a molar magnetization M related to H through^[9]

$$\frac{\partial M}{\partial H} = \chi . \quad (1.1)$$

When the magnetic field H is weak enough and χ is independent of H , then the magnetic susceptibility χ can be written as^[9]

$$M = \chi H . \quad (1.2)$$

In principle χ is the algebraic sum of two contributions:

$$\chi = \chi^D + \chi^P \quad (1.3)$$

where χ^D and χ^P represent the diamagnetic and paramagnetic susceptibilities, respectively.^[9]

Materials are classified as diamagnetic if they are repelled by a magnetic field and paramagnetic if they are attracted by the field.^[10] Diamagnetic systems do not contain any unpaired electrons and exhibit negative, rather small molar susceptibilities. Diamagnetic susceptibility χ^D is independent of the strength of the magnetic field and the temperature.^[9,11] In contrast, paramagnetism is a property of compounds containing unpaired electrons and paramagnetic susceptibility χ varies inversely with temperature, according to the Curie Law:

$$\chi = C / T . \quad (1.4)$$



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Here, χ is the magnetic susceptibility (because χ^D is much smaller than χ^P , the diamagnetic contribution can be ignored), C is called the Curie constant, T is the absolute temperature.^[11]

In paramagnetic systems, spins do not interact with each other (Fig. 1.1a). But upon being close, the spin coupling leads to a tendency towards parallel (Fig. 1.1b) or, far more commonly, antiparallel interactions (Fig. 1.1c), which is called ferromagnetic or antiferromagnetic coupling, respectively.^[5] In a ferromagnetic substance, the spontaneous ordering of spins arises in the absence of an external field and persists below a certain critical (Curie) temperature T_c . Above T_c the paramagnetic spins are uncorrelated, then the susceptibility obeys a Curie-Weiss law:

$$\chi = C/(T - \theta) \quad (1.5)$$

where the correction term θ is called the Weiss temperature (or Weiss constant) and the substance behaves as a paramagnet.^[11]

The critical temperature for the paramagnetic-antiferromagnetic transition is called the Néel temperature T_N . Analogously to ferromagnetism, above T_N the spins act as a paramagnetic system. In ferromagnetic systems the Weiss constant θ is positive, while in antiferromagnetic systems θ is negative.^[11] The plots of the susceptibility temperature product χT and the reciprocal magnetic susceptibility χ^{-1} as a function of temperature for paramagnetic, ferromagnetic and antiferromagnetic substances are shown in Fig. 1.2.

When magnetic ordering of spins arises from antiferromagnetic coupling, but because of the different spin sites there is incomplete cancellation of magnetic moments and the substance has a net magnetic moment, this kind of the collective magnetic interaction is called ferrimagnetism (Fig. 1.1d). In another case, the incomplete cancellation of magnetic moments occurs for systems with all equivalent, but to each other “canted” spins, leading to the weak ferromagnet, or canted antiferromagnet (Fig. 1.1e).^[5]

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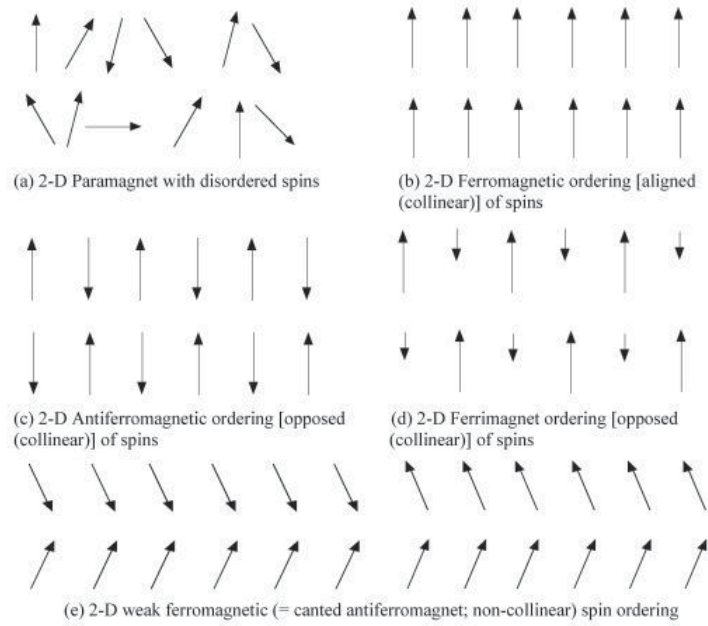


Fig. 1.1 Schematic illustrations of spin interactions for several common magnetic behaviors.^[5]

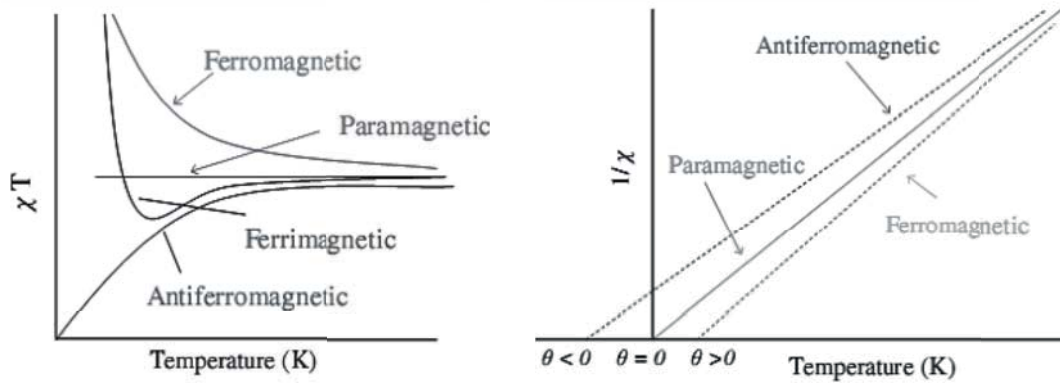


Fig. 1.2 Plots of χT (left) and χ^{-1} (right) as a function of temperature T for paramagnetic, ferromagnetic and antiferromagnetic substances.^[12]

The magnetization M for paramagnetic systems ($\theta = 0$) is given by

$$M = NgJ\mu_B B_J(x), \quad x = gJ\mu_B H / k_B T, \quad (1.6)$$

where the Brillouin function B_J is defined by



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$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right). \quad (1.7)$$

This form is known as the Curie-Brillouin law, in which N is the number of atoms (or molecules) per unit volume, g is called the g factor or the spectroscopic splitting Landé factor, J is the total angular momentum quantum number, μ_B is the Bohr magneton, k_B is the Boltzmann constant and H is the applied magnetic field.^[13]

For $x = \mu_B H / k_B T \ll 1$, the susceptibility χ is

$$\chi = \frac{M}{B} \cong \frac{NJ(J+1)g^2\mu_B^2}{3k_B T} = \frac{Np^2\mu_B^2}{3k_B T} = \frac{C}{T} \quad (\text{Curie Law}) \quad (1.8)$$

Here p is the effective number of Bohr magnetons, which is defined as

$$p \equiv g[J(J+1)]^{\frac{1}{2}}, \quad (1.9)$$

and C is the Curie constant.^[13]

If the orbital momentum is completely quenched (spin only magnetism), the Curie constant can be derived from the total spin quantum number S :

$$\chi T = C = \frac{N_A \mu_0}{3k_B} g^2 S(S+1) \mu_B^2 = \frac{N_A \mu_0}{3k_B} \mu_{\text{eff}}^2 \quad (1.10)$$

where N_A is Avogadro's number, μ_0 is the magnetic permeability of vacuum and μ_{eff} is called the effective magnetic moment with^[14]

$$\mu_{\text{eff}} = \sqrt{\frac{3k_B}{N_A \mu_0 \mu_B^2}} \sqrt{\chi T}. \quad (1.11)$$

When all magnetic domains are completely aligned with the applied magnetic field H , we speak of saturation of magnetization. The Brillouin function

$$\frac{M}{M_{\text{sat}}} = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S} \frac{gS\mu_B H}{k_B T}\right) - \frac{1}{2S} \coth\left(\frac{gS\mu_B H}{k_B T}\right) \quad (1.12)$$

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is used to describe this saturation effect with the M_{sat} defined as $M_{\text{sat}} = N_{\text{A}} g S \mu_{\text{B}}$ (Fig. 1.3).^[14]

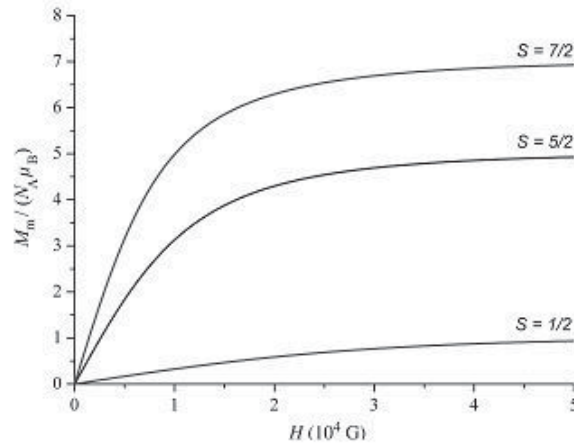


Fig. 1.3 Brillouin functions describing the saturation of the magnetization for $S = 1/2$, $S = 5/2$ and $S = 7/2$ centers in an applied magnetic field at $T = 2.0$ K.^[14]

1.3 Single molecule magnets (SMMs)

Single molecule magnets (SMMs) are a class of molecular metal clusters, which exhibit superparamagnetic-like properties, such as magnetization hysteresis loop and out-of-phase ac magnetic susceptibility signals with the oscillating magnetic field, which indicates a slow magnetic relaxation at low temperature.^[15]

When a magnetic center has a ground state $S > 1/2$ and $(2S+1)$ spin levels of spin multiplicity, its coupling with the excited states through the spin-orbit coupling may lead to a splitting into $(2S+1)$ energy levels even in the absence of an applied magnetic field. This effect is called zero-field splitting (ZFS).^[9] Herein, each energy level is characterized by a spin projection quantum number m_s , where $-S \leq m_s \leq S$, and has an energy given as $E(m_s) = m_s^2 D$, where D is called the zero-field splitting parameter or the uniaxial anisotropy. Since D is negative, the energy levels with

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$m_s = \pm S$ will lie lowest and there will be a potential-energy barrier ΔE between the $m_s = -S$ and $m_s = S$ states, which is proportional to $S^2|D|$ (integer spin) or $(S^2 - 1/4)|D|$ (half-integer spin) (Fig. 1.4). Therefore, in order to observe a slow magnetic relaxation in SMMs, it is necessary to have a high spin ground state S and a large negative ZFS of the ground state ($D < 0$).^[8,15a,16]

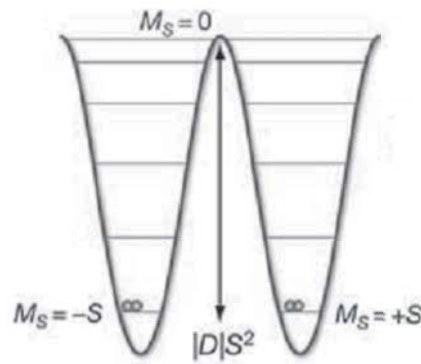


Fig. 1.4 Energy levels for a ground state S experiencing the ZFS and the energy barrier ΔE between the $m_s = -S$ and $m_s = S$ states.^[16b]

The slow relaxation of magnetization is usually characterized through ac magnetic susceptibility measurements. The ac magnetic susceptibility is measured using a small ac magnetic field with or without an applied dc field. At high frequencies, the magnetization of the compound will lag behind the drive field, causing the phase shift φ , from which both of the in-phase, real component χ' and the out-of-phase, imaginary component χ'' of the ac magnetic susceptibility are determined:^[14]

$$\chi' = \chi \cos \varphi; \quad \chi'' = \chi \sin \varphi; \quad \chi = (\chi'^2 + \chi''^2)^{1/2}. \quad (1.13)$$

The in-phase and out-of-phase ac susceptibility can be plotted against temperature at different frequencies or against frequency at different temperatures (Fig. 1.5). When

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there is a single relaxation process in the system, the χ'' vs T plot will display a peak with a maximum value at a certain temperature T , where the switching frequency matches the rate of the magnetic relaxation ($1/\tau$), and this peak will shift to higher temperature with increasing switching frequency and may follow an Arrhenius law:

$$\tau = \tau_0 e^{(U_{\text{eff}}/k_B T)} \quad (1.14)$$

allowing the energy barrier U_{eff} and relaxation time τ_0 to be estimated for a SMM.^[17]

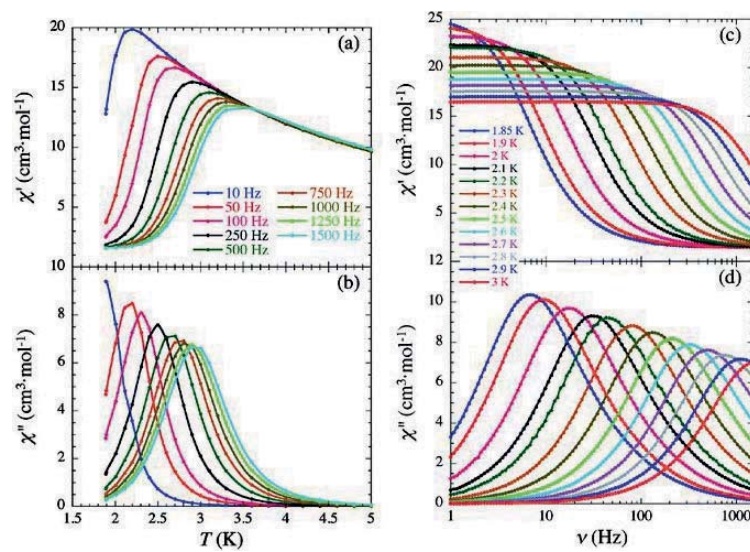


Fig. 1.5 An example of temperature dependence of in-phase χ' (a) and out-of-phase χ'' (b) ac magnetic susceptibility at different frequencies, and frequency dependence of in-phase χ' (c) and out-of-phase χ'' (d) ac magnetic susceptibility at different temperatures.^[18]

In addition, a magnetic hysteresis loop can also be observed at low temperature for a SMM. This hysteresis differs from those of the macroscopic multidomain magnetic particles and single domain nanoparticles (Fig. 1.6). The steps on each side of the hysteresis loop (Fig. 1.6, right) results from a loss of spin polarization, which results from quantum tunneling of the magnetization (QTM). This tunneling effect can only occurs when the energy levels with $m_S = S$ and $m_S = -S$ in Fig. 1.4 are resonantly

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aligned with each other, since then the levels have similar energy. The rate of the QTM is attributed to the transverse anisotropy E of the SMM.^[17]

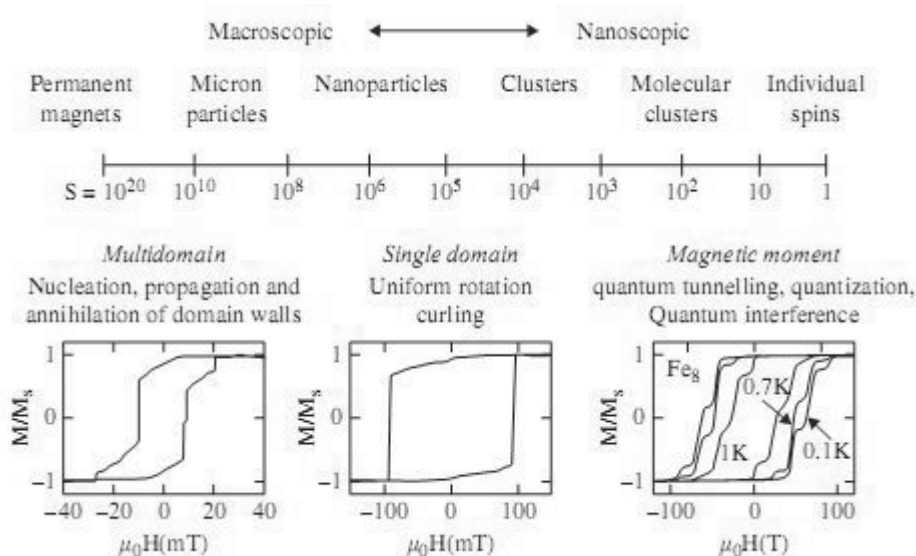


Fig. 1.6 The hysteresis loops of macroscopic multidomain magnetic particles (left), single domain nanoparticles (middle) and SMM (right).^[19]

Since the discovery of the first SMM $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$,^[7] a large number of compounds based on $3d$ transition metals displaying single-molecule magnetism have been synthesized and characterized.^[8,20] It was recognized that the behavior of SMMs depends on the parameters of spin ground state S and the magnetoanisotropy D . This implies using the strategy of increasing the total spin quantum number S in the synthesis of high-nuclearity clusters,^[21] or that of increasing the magnetic anisotropy, often by using rare earth metal ions in the preparation of new generations of SMMs.^[22,23] Lanthanides with the $[\text{Xe}]4f^n5d^16s^2$ electronic configuration have an extremely stable oxidation state of +3. Due to the shielding of unpaired electrons in internal $4f$ orbitals, the exchange interactions of the $4f$ orbitals with those of the ligands are very weak. Compared to the $3d$ transition metals, the ligand field effects for $4f$ electrons are smaller and the coupling between the spin and orbital angular

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moments are stronger. As a result of the large unquenched orbital angular momentum, $4f$ ions exhibit large single-ion magnetic anisotropies, leading to significant energy barriers in lanthanide-based SMMs. Since Ishikawa *et al.* reported a mononuclear compound, $(\text{Bu}_4\text{N})[\text{Tb}(\text{Pc})_2]$, in 2003,^[22] which displays slow magnetic relaxation below 50 K, many further $4f$ clusters or $3d$ - $4f$ mixed-metal clusters have been reported in recent years.^[23]

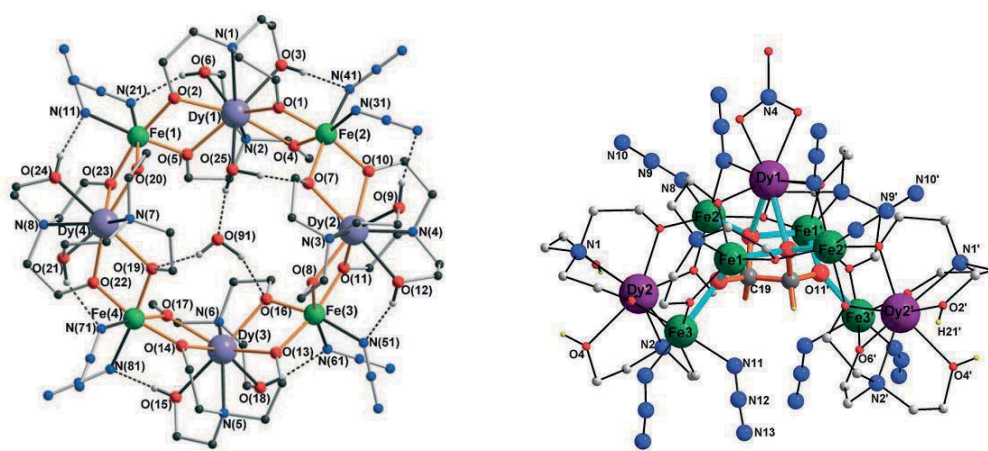


Fig. 1.7 Molecule structure of $\{\text{Fe}^{\text{III}}_4\text{Dy}^{\text{III}}_4\}$ ring^[28a] (left) and $\{\text{Fe}^{\text{III}}_6\text{Dy}^{\text{III}}_3\}$ cluster^[28b] (right).

Although there are a large numbers of reports on $\text{Cu}^{\text{II}}\text{-Ln}^{\text{III}}$,^[24] $\text{Ni}^{\text{II}}\text{-Ln}^{\text{III}}$,^[25] $\text{Co}^{\text{II}}\text{-Ln}^{\text{III}}$ ^[26] and $\text{Mn}^{\text{III}}\text{-Ln}^{\text{III}}$ ^[27] magnetic systems, the studies on synthesis and characterization of $\text{Fe}^{\text{III}}\text{-Ln}^{\text{III}}$ systems are relatively less developed,^[28] since the high spin Fe^{III} ion is isotropic and the exchange interactions in such systems are either antiferromagnetic or very weak. The first report on $\text{Fe}^{\text{III}}\text{-Ln}^{\text{III}}$ clusters involving ferromagnetic interactions was published by Powell *et al.* in 2010.^[28a] This $\{\text{Fe}^{\text{III}}_4\text{Dy}^{\text{III}}_4\}$ ring displays SMM behavior below 4 K with an energy barrier for reversal of magnetization of 30.5 K (Fig. 1.7, left). The $\text{Fe}^{\text{III}}\text{-Ln}^{\text{III}}$ SMM with the highest energy barrier has been reported