Introduction to Single Molecular Magnet

Name: Nirmal Ghimire
E-mail: nghimire@utk.edu
Instructor: Elbio Dagotto
Solid State Physics II, Spring 2010
Department of Physics and Astronomy
University of Tennessee at Knoxville

March 16, 2010

Abstract

Single Molecular Magnets(SMMs) have become attractive prospect in the last few years because of their unique quantum properties. These complexes exhibit magnetization hysteresis loops and temperature independence of the relaxation time at low temperatures indicating rich physics behind them. Phenomena of quantum tunneling and magnetization relaxation are discussed in this paper. Origin of the magnetic behavior is discussed with reference to two highly studied SMMs Mn12ac and Fe8.

1   Introduction

Origin of magnetism has its root cause in the arrangement of electronic spin in the atomic level. At least fourteen different magnetic behaviors have been identified in solids[13] , the most common types being dia, para, ferro, ferri and anti-ferro magnetism. Traditional magnetic materials are two and three dimensional array of inorganic atoms, composed of transition metal or lanthanide metal containing spin units. In 1993 it was found for the first time that an organic/inorganic molecular cluster exhibited magnetic property[1] . Later on magnetism was observed also in other molecular clusters of varying nuclearity, topology and peripheral ligation but containing various transition metals ions like V, Co, Fe, Ni and Mn . When these molecules are magnetized by application of external magnetic field, they retain the magnetism for several days. These molecules which show slow relaxation of magnetization of purely molecular in origin are termed as single molecular magnets.

Understanding between classical and the quantum world requires a study of quantum system with complexity[3]. In general, they are chosen not too small and not too large to make the passage from quantum to classical possible. These intermediate scales between the quantum microscopic and classical macroscopic are said to be mesoscopic. The importance of SMMs lies in the fact that these molecules show properties intermediate between those of simple paramagnets in microscopic regime and the classical bulk magnets in the macroscopic scales. These molecules are of nano-scale dimensions ~ 1.5 nm in diameter and they represent the point at which the classical and quantum world meet because they are macroscopic entities which display quantum effects[8] .

SMM exhibit hysteresis loop at low temperature, the close examination of which predicts quantum phenomena, the quantum tunnelling. This paper starts with the brief review of classical magnetism and general description of different aspects of single molecular magnets. Phenomenon of quantum tunneling is discussed based on the paper by Gatteschi and Sessoli[12] and origin of the magnetism is presented in two most commonly studied single molecular magnets Mn12ac and Fe8 .

2 Magnetism

On the atomic level there exist two fundamental types of magnetism: diamagnetism and paramagnetism. All the other complex magnetic behaviors evolve from these basic magnetic phenomena. Diamagnetic substances are characterized by the repulsion in a direction opposite to the applied magnetic field. Diamagnetism arises form the interaction of the applied field with the orbital containing paired electrons. Paramagnetism, on the other hand, is characterized by the attraction of a substance into an applied magnetic field. Paramagnetism arises due to the interaction between magnetic field and unpaired electrons in atomic or molecular orbital. Typically, paramagnetic materials contain one or more unpaired electrons, and the strength of paramagnetic interactions are temperature dependent. The unpaired nonzero spin angular momentum associated with an unpaired electron gives rise to a magnetic moment. Pairing of electrons within orbital results in no net magnetic moment. In general, bulk magnetic properties arise as a result of long-range interactions between unpaired electrons. These interactions can create materials that are either magnetic or non-magnetic, depending on how adjacent magnetic spins align with each other.

Yet, there is another kind of paramagnetic behavior exhibited by some metals which arises on the application of magnetic field that can be realized in a free electron gas mode. The density of states of free electron gas in absence of external magnetic field has equal number of up spins and down spins. On application of magnetic field in the direction of up spins the energy of down spin density of states is lowered whereas that of up spin density of stated is raised by equal amount. As a result, there is a spill-over of electrons form up spin to down spin until the Fermi level of electrons of up and down spins are equal, thus creating unequal number of up spin and down spin electrons which results in the net magnetic moment in the direction of the field. Paramagnetism of this kind is called Pauli paramagnetism and is independent of temperature.

Magnetism observed in a single molecule has different origin than that of the classical magnetism. SMMs are nano clusters in which each molecular unit can contain as few as two and up to several dozens of paramagnetic ions (spins). A single molecular magnet has an appreciable potential barrier for reversal of the direction of magnetization. In other words, if the magnetic moments of individual molecules in a crystal of a SMM are aligned parallel to an external field, the temperature is lowered, and the field removed, the SMM would remain magnetized with parallel spins at low temperatures. There are two basic requirements in order for a molecule to function as SMM. First, the ground state of the molecule should have a large spin S. Second, there need to be considerable negative anisotropy present[7] .

3 Quantum Tunneling and Magnetic Relaxation in System with Large Spins

If a quantum particle is confined in a symmetrical double well, the wave function of the particle in one of the well extends to the other well and vice versa, because of which there is always finite probability of finding the particle in, say, right well if it is confined in the left well. Thus, it appears that as if the particle could pass form one to the other without climbing the barrier. This quantum mechanical effect is called tunnelling. The tunnelling probability depends exponentially on the barrier height and the mass of the particle. Therefore, this phenomenon is more likely to be observed in small particles and at low temperature. Description of such a phenomenon requires that state of the particle be described by the superposition of the wave functions describing the particle in both the wells. The probability of
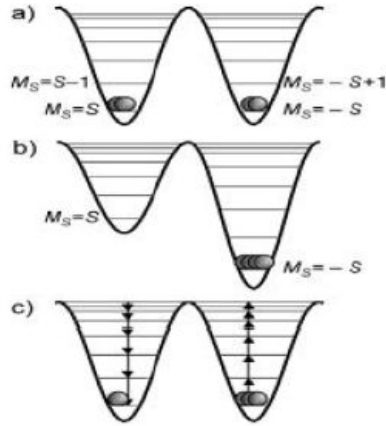
Figure 1: Energy levels for a spin state S with easy axis magnetic anisotropy a) in zero field b) with magnetic field applied c) after removing magnetic field[6]

tunneling thus depends on the extent of the interaction between the wave functions. This interaction of the wave functions results in the splitting of the two degenerate levels in the left and right wall giving rise to tunneling splitting. One of the coupled gets lowered and the other gets lifted from the unperturbed level. Difference in the energy between these two levels gives the tunneling splitting.

Another important factor affecting the tunneling is the interaction of the particle with the environment. Strong coupling between the particle and the environment leads to the localization of the particle, whereas weak coupling allows the particle to oscillate between the two states (minimas) giving rise to coherent tunneling. In case of intermediate coupling, the particle tunnels but jumps incoherently from one well to the other. These interactions can be realized in the sense that a unperturbed Hamiltonian gives the description for the two equivalent wells. Interaction between the states can be described by introducing a perturbation Hamiltonian H_1. Still another perturbation Hamiltonian H_2 is needed to take into account the coupling between the particle and the environment. Actual form of these Hamiltonians, however, depends on the nature of the system taken into consideration.

With this general description about the quantum tunneling, let us now come to the system of interest - the single molecular magnets. Their characteristic features are large ground state spin and negative anisotropy energy. Let us consider ground state spin S to be 10. The unperturbed Hamiltonian, thus

includes the effect of external magnetic field parallel to the unique axis of the cluster and the effect of its axial splitting as result of crystal-field effects. Therefore, the unperturbed Hamiltonian takes the form

$$H_o = D[S_z^2 - \frac{S(S+1)}{3}] + g\mu_B H_z S_z \qquad (1)$$

where, D is a negative constant representing the parameter of zero-field splitting (ZFS) that removes the degeneracy of the S multiplet. H_z is magnetic field strength in z-direction. Energy of the spin level corresponding to H_o is given by

$$E = D(M_s^2 - \frac{110}{3}) + g\mu_B H_z S_z \qquad (2)$$

where, -S $\leq$ Ms $\leq$ S.

The energy level can be plotted as shown in figure 1. In absence of external magnetic field, the energy levels are degenerate pairs except for that corresponding to level Ms = 0. As D is negative, the lowest levels are $\pm S$. When field is applied, the energy level of $+M_s$ and -M_s levels change. The lowest lying energy level being the state -S i.e S = -10 in this case. When the external field is removed, the system must go back to the thermal equilibrium i.e. at the equilibrium, half of the molecule must be in M_s = -10 and half must be in M_s = +10 resulting in no net magnetization. The phenomenon of returning to the equilibrium is known as relaxation. Magnetization in terms of time can be the measure of relaxation. The process of relaxation can be realized in terms of spin-phonon coupling. By coupling to vibration, a molecule can change its state from M_s = -10 to M_s = -9 by absorbing one quantum which corresponds to the difference in energy between these states . This process can be repeated to go up to M_s = 0. From this, the spin can lose its energy by emitting phonons to reach M_s = +10 state. The relaxation rate is described by Arrhenius law :

$$\tau = \tau_o e^{\frac{\Delta E}{K_B T}} \qquad (3)$$

where, τ is relaxation time, τ_o is the characteristic time of the material which, depends on the value of spins and the magnetic anisotropy energy. Large relaxation time requires large S and large zero-field splitting.

At low temperature, the system is in the degenerate state. So in external field only transition from the ground state occurs. At higher temperature, the particles are distributed in levels. It is found that below a threshold frequency called the blocking temperature, pure quantum tunneling occurs[10].

So far, we were talking about the unperturbed Hamiltonian Ho, the term that commutes with S_z. For tunneling a perturbation Hamiltonian H_1 must be introduced. A common form for H_1 is:

$$H_1 = E(S_x^2 - S_y^2) \tag{4}$$

Since H_1 does not commute with H_o, the total Hamiltonian $H = H_o + H_1$ are an admixture of $|\ M_s >$ states with different sign of M, thus meeting the criteria for tunneling. H_1 mixes levels of S = M and S = M±2 as a result, transition would occur between these two states.

On application of magnetic field in the z-axis, the degeneracy in ±Ms levels will be removed. But there may occur resonant tunneling under the condition

$$H_z(n) = nD \tag{5}$$

where,$D' = \frac{D}{g\mu_B}$ and n = 0,1,2,...

More interestingly, when field is applied along the hard axis oscillatory behavior of tunnel splitting is observed (figure 2). At zero field, the two levels split by an amount which depend on $\frac{E}{D}$. When field is increased, the splitting decreases and become zero at $H_x = \sqrt{E'(D' + D'}$ where, $E' = \frac{E}{g\mu_B}$ and $D' = \frac{D}{g\mu_B}$. Again, field is increases on increasing the field and become maximum at $H_x = 2\sqrt{E'(D' + D'}$. The splitting then decreases with the field. The oscillation repeats until the field reached a value of

$$H_x = (2n + 1)\sqrt{E'(E' + D')} \tag{6}$$

beyond which there will be no more splitting.

If transverse field is applied together with a field in the z-direction, the oscillating behavior is still observed and there appear parity effects, as a result, equation 7 is valid only for even n. For odd n, the condition for quenching will be[12]:

$$H_x = \sqrt{E'(E' + D')} \tag{7}$$

4   Mn12ac and Fe8 as Single Molecular Magnets

High spin molecular magnets Mn12 and Fe8 have been actively studied as model system for the behavior of the mesoscopic spins. These molecules
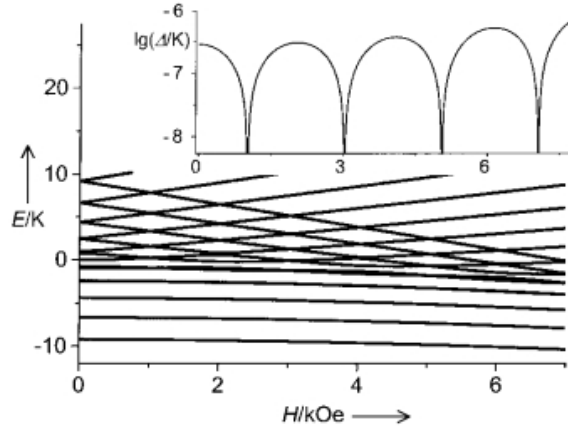
Figure 2: Oscillatory behavior of tunneling splitting[12]

are weakly interacting nano-magnets with net spin S = 10 and strong uni-axial anisotropy. They provide a unique opportunity to study the interplay between classical thermal activation and quantum tunneling of magnetization. Of particular interest are the observations of regular series of steps and plateaus in magnetic hysteresis loop at well defined intervals. These steps correspond to enhanced relaxation of magnetization and their temperature dependence suggests that quantum tunneling is important to the magnetization reversal. Mn12ac is the name given to the compound $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4].2CH_3CHOO.4H_2O$. The schematic representation is shown in figure 3. This molecule has a tetragonal symmetry[14]. The Mn12ac manganese ions are divided into two layers: eight of spin 2 and four of spin $\frac{3}{2}$ with strong anti parallel coupling. They form a collective spin S = 10 with magnetic moment $m \simeq 20\mu_B$. The Mn12 atoms are separated from each other by disordered acetic acid molecules and water of crystallization. Intermolecular exchange interactions are forbidden and dipolar interactions are weak. The anisotropy barrier for each molecule is about 65K or 9.6T[4].

The overall antiferro magnetic coupling in Mn12ac can be realized by the temperature dependence of χmT (figure 4). The fact that the value of χmT at room temperature (19.4 emu mol^{-1} K) is smaller than that expected for uncoupled spins (31.5 emu mol^{-1} K) indicates antiferromagnetic coupling. The maximum χmT (55.6 emu mol^{-1} K) observed at low temperature is close to the value for spin S =10. The confirmation, however, comes from high field (HF) magnetization studies[12]. The evidence for
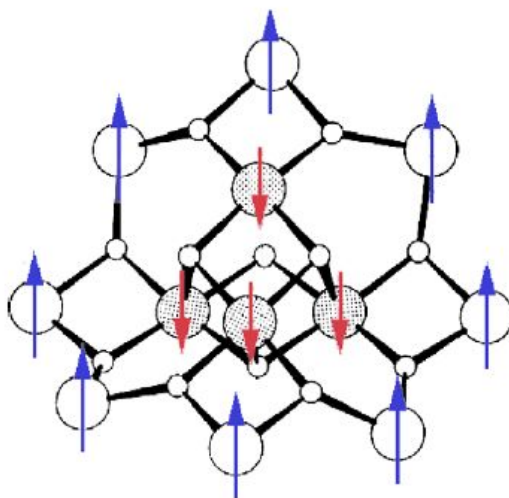
Figure 3: Schematic representation of the Molecule Mn12ac[4]

magnetic anisotropy along the easy axis has been provided by single crystal magnetization (figure 5). The fact that the parallel (to the tetragonal axis) magnetization reaches saturation much more rapidly than the perpendicular magnetization indicates a strong Ising anisotropy[15].

Figure 6 shows the temperature dependence of relaxation time up to 2.1 K. The relaxation time is found to follow the exponential law. These relaxation effects are consistent with large anisotropy in the susceptibility confirmed by anisotropy measurements . Electron paramagnetic resonance spectra indicated that a large zero field splitting with M=10 levels lying lowers in energy and the M $=$ 9 levels at $\sim$10 cm^{-1}. Only the lowest levels are populated
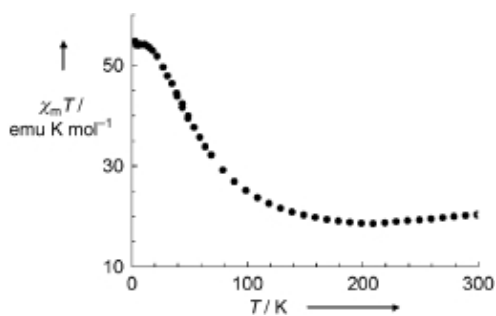

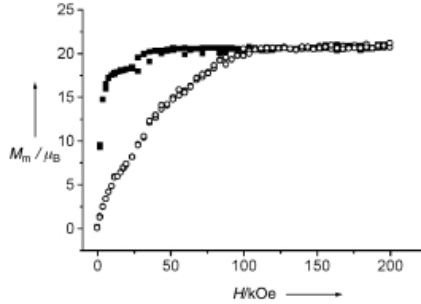Figure 4: Temperature dependance of $\chi_m T$ for Mn12ac[12]

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Figure 5: High field magnetization for a single crystal of Mn12ac with magnetic field parallel (solid circle) and perpendicular(open circle) to the tetragonal axis[12]
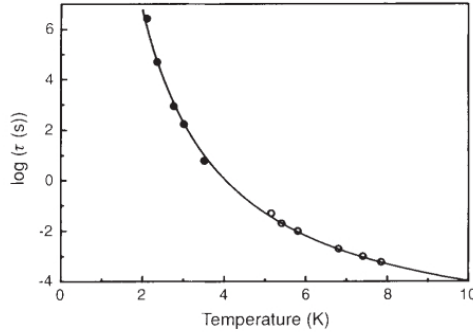

Figure 6: Temperature dependance of relaxation time for Mn12ac[9]

at low temperature and they are responsible for the large observed Ising anisotropy[2].

The cluster of Mn12ac shows a clear hysteresis loop as shown in figure 7. It is seen that below the blocking temperature there are unusual stairs. The steps occur at well defined fields $H_n = n0.4T$ where, n=0, 1, 2, ... This provides the evidence for quantum tunneling because at the given field, there are pair of energy levels with the same energy [11] In the flat portion of the loops the relaxation time is much larger than the measuring time scale (t_m) and in the steep portion of the loop where M relaxes rapidly $t_m \simeq \tau$. This hysteresis is substantially different from that of an ordered magnetic material. Unlike the hysteresis in ferromagnetic materials where the effect of applied fields is responsible for the movement of the domain walls, the
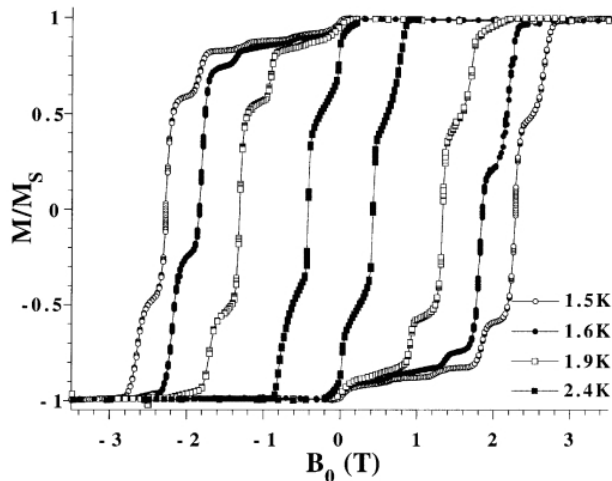
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Figure 7: Hysteresis loop of magnetization for Mn12ac[4]

hysteresis curve here arises due to acceleration of relaxation by the field. The reversibility field decreases with increasing temperature[9].

Often the final proof for quantum tunneling is associated with the temperature independence of the relaxation time. This limit is never reached experimentally for Mn12ac because below 2K τ becomes experimentally long (figure 6) and hence reliable measurements become practically impossible[12]. Another highly studied single molecular magnet is Fe8. The formaula is $[Fe_8O_2(OH_{12}(tacn)_6)Br_8$ (tacn = 1,4,7 - triaza-cyclononane). Figure 8 shows the schematic structure of Fe8. The temperature dependence of χT clearly indicates the behavior of S = 10 state. This ground state can be realized by putting six S $= \frac{5}{2}$ spins up and two down. Magnetic anisotropy in Fe8 is assumed to have dipolar and single ion contribution. However, as the dipolar contribution is small, single ion contribution alone is relevant[12]. Figure 9a shows the temperature dependence of the relaxation time of magnetization of Fe8. It has been observed that relaxation time becomes temperature independent below 400 mK which confirms the presence of pure quantum tunneling[5]. The hysteresis loop is quite similar to that of Mn12ac (figure 9b), also with equidistant magnetization jumps. As with the relaxation time, hysteresis becomes temperature independent below 350 mK that makes Fe8 better
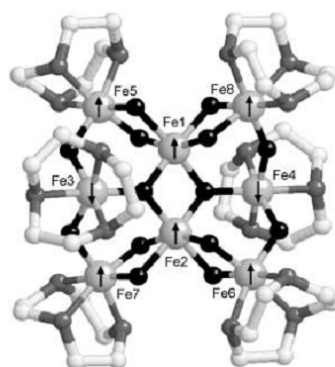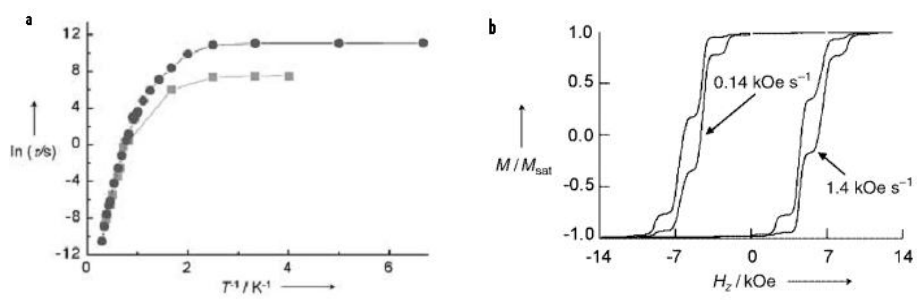
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Figure 8: Schematic structure of Fe8[12]

Figure 9: a)Temperature dependance of relaxation time for Fe8 (dark circles) b)Hysteresis loop for Fe8[12]

suited for the study of effects related to tunneling process[12]. There are many other molecules showing the behavior of SMM. Some of them are Fe4, Mn4, V4, CrM6, Ni12, and Mn10. It has been realized that size of the cluster is not important for the behavior of SMM. The important factors are the ground state spin S and the magnetic anisotropy. All these molecules are reported to show slow relaxation at lower temperature than Mn12ac[12].

5 Conclusions

Single molecular magnets have opened an avenue for the study of physical phenomena at the interface between the microscopic quantum world and the macroscopic classical regime. Experimentally, SMMs provide a signature of quantum mechanical behavior such as quantum tunneling in macroscopic systems which is derived from a combination of large spin (S) and easy axis magneto-anisotropy. SMMs also have the application aspect such as in quantum computation. The effort has been in developing the SMMs with higher blocking temperature for the viable use in the future generation quantum computers and magnetic data storage. Various experimental techniques have been successfully used for the investigation of these systems, however, there is still need of neat theory to describe them.

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