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Single molecule magnets: a new class of magnetic materials

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Abstract

Recently it has been discovered that some molecules comprising a large number of coupled metal ions show slow relaxation of the magnetization at low temperature. This gives rise to magnetic hysteresis effects of molecular origin which in principle allow the storage of information in a single molecule (Single molecule magnets). A short overview of the current status of research in this field is provided.

Keywords: Single molecule magnets; Molecular magnetism; Quantum tunneling of the magnetization; Molecular clusters; Spin clusters

1. Introduction

Magnets are widely used for a large number of applications, and their market is larger than that of semiconductors. Information storage is certainly one of the most important use for magnets, as it is realized in tapes, hard disks, floppy disks, etc. Like in all the information technologies there is a tendency to reduce the size of the magnetic memory elements, using smaller and smaller particles. However there is a lower limit to the size of the particles, provided by the superparamagnetic size, below which the information cannot be permanently stored, because the magnetization freely fluctuates. For a magnetic particle with easy axis anisotropy the magnetization can be oriented either ‘up’ or ‘down’. The reorientation of the magnetization occurs by overcoming a barrier, the anisotropy barrier, which is proportional to the volume of the particle. When the volume is small enough the magnetization freely fluctuates (superparamagnetic limit). This occurs at room temperature for particles of the size 10–100 nm due to the nature of the material. However even smaller particles can in principle be used either by working at lower temperatures or by taking advantage of the onset of quantum size effects, which can make magnetic particles candidates to be used as hardware for quantum computers, as will be briefly stated below.

Recently it has been discovered [1–5] that molecules containing several transition metal ions show slow relaxation of the magnetization at low temperature, behaving like superparamagnets below the blocking temperature. This is a very interesting property, because they give rise to magnetic hysteresis effects, of molecular origin, therefore becoming bistable [2]. The possibility is therefore open to store information in a single molecule. In order to stress this possibility the expression single-molecule magnets (SMM’s) [6] has been introduced. It is necessary to clarify from the beginning that this term is evocative, but is not correct: a magnet is characterized by the divergence of the spin correlation length, which of course cannot occur in a finite system.

An overview of the ongoing research on SMM’s is presented in this review, with the goal of showing the factors determining their magnetic properties and giving some indication of possible applications.

2. Examples of single-molecule magnets: Mn12

In 1993, the compound $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2CH_3COOH$ (Mn12) was discovered as the first SMM [2]. A drawing of the cluster of twelve manganese ions of Mn12 [7] is shown in Fig. 1. The eight external manganese ions are trivalent, each with four unpaired electrons, while the four internal ions are manganese(IV), each with three unpaired electrons. The cluster has a crystal imposed tetragonal symmetry. The manganese ions are bridged by oxide ions, like in bulk oxides. The difference is that the size of the particle is finite, due to the presence of the carboxylate groups which prevent their further growth. The relaxation time of the magnetization

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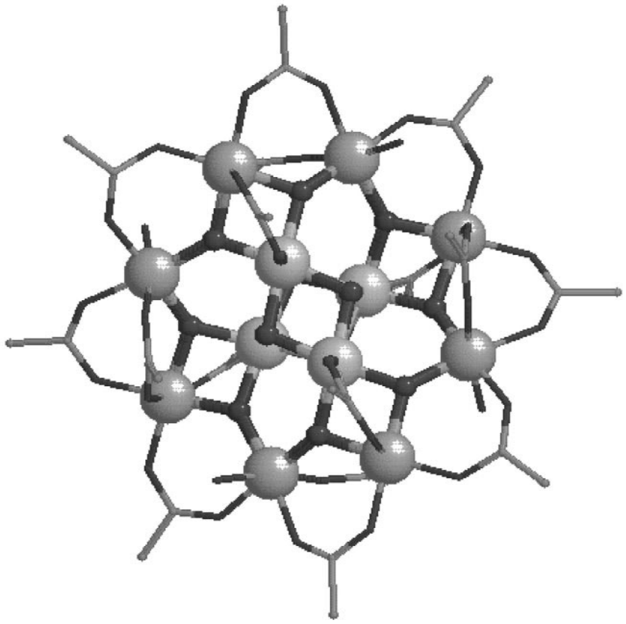

Fig. 1. Structure of $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$, Mn12. The external ring comprises eight manganese(III) ions, each with a spin $S=2$, and the internal tetrahedron comprises four manganese(IV) ions, each with spin $S=3/2$.

was found to follow a thermally activated behavior in the range 2–15 K, as shown in Fig. 2. The parameters used to fit the Arrhenius type dependence of the relaxation time of the magnetization, τ, are: $\tau_0=2.1\times10^{-7}$ cm^{-1} and $\Delta/k=62$ K. This means that the relaxation time of the magnetization of Mn12 is of the order of months at 2 K.

The origin of this behavior is the large ground spin state of Mn12, $S=10$, and the large magnetic anisotropy associated with a large zero field splitting of the ground state, which leaves the $M=\pm10$ components lying lowest [8]. The large spin ground state arises from antiferromagnetic interactions between the $S=3/2$ spins of Mn^{IV} ions and the spins $S=2$ of Mn^{III}. A simple picture of the nature of the ground state can be achieved by setting all the manganese(III) spins up and the manganese(IV) spins down. At low temperature the molecules will be in the degenerate state $M=\pm10$. If a molecule is magnetized parallel to an external magnetic field it will be in the $M=-10$ state. In order to flip the spin of a Mn_{12} molecule from along the $+z$ axis to along the $-z$ axis of the disc-like $Mn_{12}O_{12}$ core, the molecule must climb [9] all the ladder of levels from $M=-10$ to $M=0$, one step at a time, and then descend to $M=+10$. This process requires some energy corresponding to the energy difference between the $M=-10$ and the $M=0$ state in zero field. This is an easy axis type anisotropy.

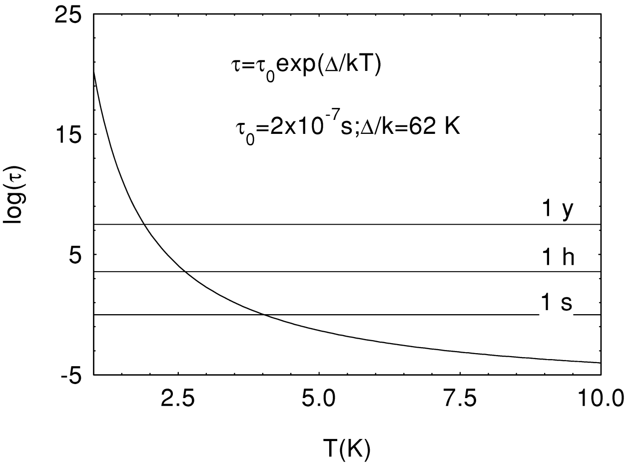

Fig. 2. Temperature dependence of the logarithm of the relaxation time of the magnetization of Mn12. The curve has been obtained by ac susceptibility measurements at the higher temperatures, and by directly measuring the time dependence of the magnetization at lower temperatures. The horizontal lines correspond to 1 second (1 s), 1 hour (1 h), and 1 year (1 y).

It has been conclusively established that the slow magnetization relaxation shown by a SMM is due to an individual molecule rather than to long range ordering as observed in nanoscale magnetic domains. Support for this conclusion comes from several experiments such as magnetization relaxation data for frozen solutions or polymer-doped samples [10], the absence of any anomaly in heat capacity measurements [11], (no long-range magnetic ordering), and MCD spectra in solution [12].

When a sample of Mn12 is magnetized by the application of a large external magnetic field, the $M=-10$ state is greatly stabilized in energy relative to the $M=+10$ state, and all the Mn12 molecules have their spins aligned with the external field. If the external field is reduced to zero the magnetization relaxes too slowly to reach the equilibrium value, corresponding to zero magnetization. A remnant magnetization is observed as the spins are frozen in the magnetized state. A negative field reduces the height of the barrier and releases the spins thus allowing a rapid reversal of the magnetization. An hysteresis loop is therefore observed, which has a molecular and dynamical origin. The size of the loop (i.e. the coercitive field) depends on the temperature, as well as the rate of sweep of the magnetic field. Large coercitive fields, of several Teslas, have been observed for Mn12 below 3 K, as shown in Fig. 3. The important feature is that at zero field the magnetization of Mn12 can be either positive or negative, depending on the history of the sample. Therefore the molecule is bistable and it is possible in principle to store information in one single molecule.

The magnetic anisotropy of the ground state of Mn12 largely results from magnetic anisotropy of the eight Mn^{III} ions. The coordination around each Mn^{III} ion is not regular octahedral, but Jahn–Teller distorted due to the ground ^5E_g state such that two bonds are longer than the other four (called a Jahn–Teller elongation). These ‘crystal-field’ distortions together with a spin–orbit interaction establish a zero-field interaction at each Mn^{III} ion. Thus, it is the vectorial projection of single-ion anisotropies on to the

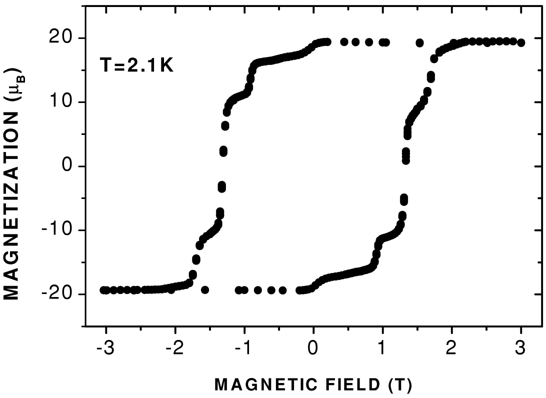

Fig. 3. Hysteresis loop for a single crystal of Mn12 at 2.1 K. The horizontal segments correspond to fields at which the magnetization relaxes comparatively slowly, the steep segments correspond to fields at which comparatively faster relaxation is operative.

ground $S=10$ state that gives rise to the easy axis type magnetoanisotropy.

The hysteresis loop of Mn12 shows some additional features [13,14] in the form of steps, which are not usually observed in classic magnets. The steps occur at well defined fields, $H_n=n$ 0.4 T, where $n=0, 1, 2, \dots$ This has been taken as the evidence for a tunnel mechanism, because at the given fields there are pairs of levels with the same energy. Under these conditions the pairs of levels can be quantum admixed and tunneling may result provided the coupling is sufficiently strong. The coincidence of levels occurs at zero field, because under these conditions the $\pm M$ pairs are degenerate. When a field is applied the energies of the $+M$ levels increase and those of the $-M$ levels decrease, thus reducing the effectiveness of the tunneling mechanism. At a given field H_n however the $-M+n$ level will meet the $+M$ level, thus restoring the conditions for quantum tunneling. The crossing fields can be easily calculated from the energies of the levels, which are accurately known in zero field and they compare very well with experiment.

In order to have sizable tunneling effects it is necessary that there is a large transverse field in the molecule. In fact the two states contributing to the tunneling must be quantum admixed, and this can be achieved only if a transverse anisotropy is present. The transverse anisotropy is rather small in Mn12, because the molecule has tetragonal symmetry, which means that a transverse anisotropy is only present in high order. If the crystal-field effects are expanded in a series of multipolar terms, the transverse anisotropy is zero in the quadrupolar term, and only hexadecupolar terms do introduce an anisotropy. The tunneling mechanism therefore must be particularly inefficient in Mn12, and in fact the regime of temperature independence of the relaxation of the magnetization, which can be considered as the signature of quantum tunneling, is never achieved.

Recent experiments [15] have suggested that the assistance of the fluctuating fields generated by the magnetic nuclei, like ^{55}Mn are responsible for the relaxation mechanism of Mn12 at very low temperature.

3. Another SMM: Fe8

Shortly after the discovery of the novel magnetic properties of Mn12 another molecular cluster was observed [16,17] to behave in a similar way. This is a cation with eight iron(III) ions, $[Fe_8(tacn)_6O_2(OH)_{12}]^{8+}$, Fe8, where tacn=1,4,7-triazacyclononane [18]. A sketch of the structure of the cation is shown in Fig. 4. The anions in the original form are bromide ions. Also, in this case the inner core of the molecule is similar to that of an iron oxide (hydroxide), but the presence of the organic molecules prevents the growth of the particles to form infinite lattices. The iron ions are in the trivalent state, each with spin $S=5/2$, and the cation has a ferromagnetic ground state also characterized by $S=10$. A simple scheme of the spin density is sketched in Fig. 4. The nature of the ground state was recently confirmed by polarized neutron diffraction data [19]. The ground state is largely split by crystal-field and exchange effects, in such a way that the $M=\pm10$ components lie lowest. The main difference with Mn12 is that the overall splitting of the ground $S=10$ state is about one third that of the manganese cluster, and also that the transverse anisotropy is much larger in Fe8, because the cation has no symmetry. The result is that the relaxation time of the magnetization of Fe8 is much faster than that of Mn12 at all temperatures, and that the tunneling mechanism is much more efficient. In fact the regime of

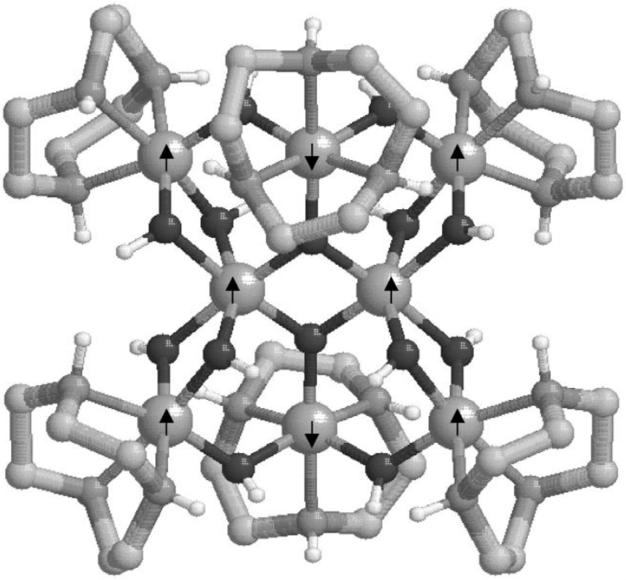

Fig. 4. Sketch of the structure of $[Fe_8(tacn)_6O_2(OH)_{12}]^{8+}$, Fe8. The larger spheres correspond to iron(III) ions with spin $S=5/2$. The arrows describe the preferential arrangement of the spins determining a ground spin state with $S=10$.

temperature independence of the relaxation rate of Fe8 is achieved below 300 mK, where it can be safely assumed that the relaxation occurs essentially via a tunneling mechanism [17]. Therefore Fe8 is really so far the best system to investigate in detail the mechanism for tunneling of the magnetization.

The way the molecules undergo tunneling is still a matter of debate, but evidence is accumulating in favor of the mechanism to be discussed below. If only second-order (quadrupolar) terms are present the $M=\pm10$ levels are degenerate in axial symmetry. If the symmetry is lower than axial, the $(S_x^2-S_y^2)$ operator mixes the two states and tunneling is possible. The two levels are split by the transverse field H_t and the magnetization can fluctuate with a frequency proportional to Δ, the tunnel splitting [20]. The tunnel splitting of Fe8 is of the order of 10^{-9} T, much smaller than the dipolar field, H_d, generated by the other molecules in the crystal lattice. In Fe8, H_d is of the order of 1–10 mT, therefore at this level of approximation the condition for tunneling is not met. However the above picture neglects the role of the magnetic nuclei present in the cluster. The ^{1}H ($I=1/2$), ^{14}N ($I=1$), ^{79,81}Br ($I=3/2$) nuclei generate a fluctuating hyperfine field, H_{hy}, at the magnetic centers broadening the $M=\pm10$ levels. The broadening is of the order of 1 mT and it may restore the tunneling conditions for the molecules for which $H_d<H_{hy}$. However, since the distribution of dipolar fields is larger than that of hyperfine fields, the process should soon stop. In order to justify the observed continuous quantum relaxation to thermal equilibrium it must be considered that when a molecule tunnels it changes its magnetization and therefore the dipolar field felt by the neighboring molecules creating regions in the sample where the condition $H_d<H_{hy}$ is met.

Another way of imposing the condition that the tunnel splitting is larger than the local fields is to apply a field perpendicular to the easy axis. The applied field will increase the tunnel splitting which can then be more easily measured. In this way long-searched quantum effects were observed for the first time in magnets [21].

4. Other SMM's

From the above it is becoming clear what is needed in order to have SMM's: both large ground spin states and Ising type magnetic anisotropy and must be embedded in a molecule. Much effort has been directed recently towards this goal, and some success has indeed been obtained, but so far in systems with smaller ground spin states that $S=10$ of Mn12 and Fe8. The molecules with the highest ground spin states so far reported have $S=51/2$ [22] or $S=33/2$ [23], but in both cases the magnetic anisotropy is small and no slow relaxation effects were observed.

Other SMM's are a cluster with four iron ions [24], Fe4, and a series of clusters with four manganese ions [10]. For the former the ground state has $S=5$, while for the latter it has $S=9/2$. In both cases slow relaxation of the magnetization has been observed. The Mn_4 complex has also been shown to have a temperature-independent magnetization relaxation rate. This complex has a well-isolated $S=9/2$ ground state with $D=-0.53$ cm^{-1}. Magnetization relaxation rates were determined in the 0.394–2.00 K range. Below 0.60 K the rate becomes temperature independent with a rate of 3.2×10^{-2} s^{-1}. Above 0.60 K the rate is Arrhenius-like with an activation energy of 11.8 K. This Mn_4 complex shows magnetization tunneling in its $m_s=\pm9/2$ lowest energy levels. INS data [18] for this complex show the presence of appreciable second-order zero-field interactions, which likely play a crucial role in the tunneling.

There is one other very significant point to make about the magnetization tunneling for Mn_4. The $m_s=\pm9/2$ lowest energy levels of this $S=9/2$ complex comprise a Kramers degenerate pair in *zero magnetic field*. In zero magnetic field such a $S=9/2$ molecule cannot coherently tunnel from the $m_s=-9/2$ level to the $m_s=+9/2$ level. However, experimentally a very large step is seen at zero external magnetic field in the hysteresis loop for Mn4. It was suggested that in zero external magnetic field the magnetization tunneling observed for Mn_4 is attributable to a transverse magnetic field due to the nuclear spins of the manganese ions.

5. Perspectives

The field of molecular nanomagnetism is just at the beginning. The advantage of molecular clusters, compared to all the other types of magnetic nanoparticles, is that they are all identical to each other and their structure is known. Furthermore, intermolecular interactions in the crystal lattice are so weak that in most cases the response of the crystal is the same as that of an individual molecule. Therefore it is possible to measure a molecular response by using traditional macroscopic techniques. On the other hand, the fact that the molecules are bistable makes them interesting objects to be addressed individually. Therefore it can be foreseen that in the next few years techniques to address single molecules will be developed. The other developments to be expected are the synthesis of larger clusters, which will be investigated for a large number of different properties, which can make them appealing for biocompatability (for MRI contrast agents, for instance, or for magnetic drug delivery) and for the development of new physics. In fact, the results already obtained have shown that these materials open exciting new perspectives in mesoscopic physics. There are high expectations for the fundamental contributions that this highly interdisciplinary area can bring.

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