MOLECULAR NANOMAGNETS

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Abstract

In the seminar I will describe the enormous progress made in the field of magnetic molecules. In the last decade 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 effect of molecular origin. As we will see molecular magnets are also unique because they show quantum effects on a macroscopic scale. After introducing the concept of molecular nanomagnets I will concentrate on describing a prototype molecular nanomagnet, Mn12-ac. At the end I will tell something about future development in this field of physics.

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1. Introduction

Molecular magnetism can be defined as the interdisciplinary area where the techniques of molecular chemistry are exploited in order to design and synthesise new classes of magnetic materials. In its development it has already passed through several different steps. The first one was that of showing that purely organic magnetism is indeed possible. In the beginning of the nineties the pioneering work of Itoh and Iwamura [1] showed that strong ferromagnetic coupling could be realized in polycarbenes. Later Kinoshita [2] reported convincing evidence for the ferromagnetic ordered state of the organic nitronyl nitroxide radical. The highest critical temperature reported so far for this class of materials is 1.4 K [3]. In the middle of the nineties TDAC – C\textsubscript{60} was discovered with T\textsubscript{c} = 16 K [4].

Having established the fundamental pillars of the knowledge in the field of molecular magnetism the interest shifted in part from the race to room temperature magnets to exploiting the peculiarities of molecular magnets, which are hardly observed in classical magnets. Many efforts are currently done to design magnetic materials, which show optical activity, or the coexistence of conducting (superconducting) and magnetic properties [5].

Figure 1: The evolution of disk drives 1956 – 2002 [6]
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. Figure on the previous page shows us how the dimensions of disk drives have changed during the time period 1956-2002. We can see that there has been a dramatic change in size and in storing capacity.

At the beginning of the nineties another research area started to emerge from the same starting point, that of large organometallic molecules, comprising a large but finite number of magnetic centres (usually transition metal ions), which were shown to have magnetic properties intermediate between those of isolated paramagnets and bulk magnets. The interest for magnetic molecules, or molecular nanomagnets as they can be called, is due to the fact that they on one side show magnetic hysteresis as a bulk magnet and on the other side they are still small enough to show important quantum effects.

2. Magnetism and quantum effects

2.1 Large scale quantum behaviour

Can quantum mechanics, which determines the behaviour of light and matter at the atomic scale and below, manifest itself on a macroscopic scale? This question, which was first posed in the early days of quantum theory in the 1920s, has fascinated physicists for more than 70 years. The scenario of ‘Schrödinger’s cat’ – where the cat is described by a wavefunction that is a superposition of two states, one with the cat alive in and the other with a cat dead – is a famous example that illustrates the conceptual complexity that arise from the intermingling of the quantum and the classical regimes.

First manifestations of quantum mechanics on a macroscopic scale were the phenomena of superconductivity, discovered by Kammerlingh Onnes in 1911, and superfluidity in helium, discovered several decades later. More recently, quantum effects have been observed at a mesoscopic scale, these examples are quantum tunnelling of phase in a Josephson junction, permanent currents in a small conducting rings and Bose-Einstein condensates. In molecular nanomagnets a characteristic quantum tunnelling of magnetization can be observed on a macroscopic scale.

2.2 Principles of magnetism

Electrons are responsible for atomic magnetism. The basic unit in electron magnetism is the Bohr magneton $\mu_B$, which is defined as

$$
\mu_B = \frac{e_0 \hbar}{2m_e},
$$

(1)
where $e_0$ and $m$ are the charge and mass on the electron, $h$ is the Planck constant. The magnetic moment of the electron is given by next equation:

$$\mu_e = -g \mu_B \vec{S}.$$  \hspace{1cm} (2)

Here $g$ is the Landé $g$–factor and equals approximately 2, $\vec{S}$ is the electron spin angular momentum.

The dominant interaction between two spins is the exchange interaction. This interaction, discovered by Heisenberg, is an effect of the Pauli exclusion principle. We can write the following equation

$$\mathcal{H}_J = -J \vec{S}_1 \cdot \vec{S}_2.$$  \hspace{1cm} (3)

Here $J$ is a constant which is positive when the two spins are parallel, and negative when they are antiparallel. Such an interaction is said to be ‘ferromagnetic’. The exchange energy is usually much larger than the energy associated with other magnetic interaction, such as the ‘dipole energy’ and the ‘anisotropy energy’. For sufficiently small ferromagnetic particles the exchange energy dominates over all other interaction and all the moments point in one direction. Such particles consist of a single domain and we can define $M$, as the magnetization of the particle. Its magnitude can range from several Bohr magnetons for particles only a few angstroms in diameter to of the order of $10^5 \mu_B$ for particles with dimensions of tens of nanometres.

Dipole coupling, which accounts for the coupling between two dipole moments, has a long range. It tends to cause the magnetic moments on the surface of a magnetic material to lie in antiparallel directions. In large enough samples, typically with dimensions larger than a few tens of nanometres, dipole coupling causes neighbouring magnetic domains to point in antiparallel or perpendicular directions.

In magnetic particles the anisotropy energy tends to align the magnetization along certain crystal axes. In particular, this energy has minima along certain directions, with energy barriers separating them. Since all physical systems seek to be in the state of lowest energy, the moments tend to line up along these directions, which are referred to as ‘easy axes of magnetization’.

For a simple example we can assume that the system has only one easy axis, so there is an energy barrier, $\Delta$, between the two states in which the moment is aligned with the easy axis. In thermal equilibrium, according to classical physics, the direction of the magnetic moment of a single domain nanoparticle is constantly fluctuating, with the most likely direction being along the easy axis. Suppose that the magnetization is initially oriented along one of the two easy directions. It can reverse by using thermal energy to pass over the energy barrier.

In addition to this ‘thermal activation’, which is a classical process, a quantum process is possible – quantum tunnelling of the magnetization from one side of the barrier to the other. In principle, no thermal energy is needed because quantum tunnelling leads the system from one state to another with the same energy.
In a single domain magnetic particles with only one easy axis there are two minimum energy states, corresponding to the two directions in which the magnetic moment of the particle prefers to point along the easy axis. The two states are separated by an energy barrier. This can be seen if the energy is plotted as a function of the angle between the magnetization and one of the easy axis directions (Fig. 2). If an external magnetic field is applied parallel to the easy axis (Fig. 2.b), then the energy of one state increases, while the other decreases. This reduces the energy barrier in one direction and increases it in the other. The barrier disappears when the field exceeds a certain value called the anisotropy field $B_A$.

3. Single molecule magnets

3.1 A new class of magnetic materials

As I have mentioned in the introduction new magnetic materials could be used as a magnetic memory elements. However there is a lower limit to the size of the particles, provided by 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’, as we can see in Fig. 2. 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 anisotropy energy becomes comparable or smaller than thermal energy $k_B T$ and the magnetization freely fluctuates (superparamagnetic limit). Typically 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 advantages of the onset of quantum size effects, which can make magnetic particles candidates to be used as hardware for quantum computers.

Recently it has been discovered 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 the magnetic hysteresis effect, of molecular origin, therefore becoming bistable [7]. The possibility is therefore open to store information in a single molecule. In order to stress this possibility the expression single molecule magnets has been introduced.

### 3.2 Manganese acetate (Mn12-ac)

In the early investigation of quantum tunnelling in magnetism, the only samples that were available consisted of systems of many mesoscopic spins, such as aggregates of isolated particles, domain walls in alloys or liquid suspensions. The broad distribution of particle sizes and shapes, with a consequent distribution of anisotropy energies, made it difficult to interpret the results of experiments. The great advantage of Mn12-ac and similar systems is that it is possible to grow crystals of identical magnetic clusters.

The compound \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O} \cdot 2\text{CH}_3\text{COOH}\) or Mn12-ac was first discovered in 1980 by T. Lis [8]. However only in 1993 it was shown that Mn12-ac expresses magnetic bistability and can be regarded as a single molecule magnet [7]. A drawing of the cluster of twelve manganese ions of Mn12 is shown in Fig. 3. 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.

![Figure 3: Sketch of the structure of Mn12-ac. The hatched circles correspond to manganese(III) ions, the large empty ones to manganese(IV), the smaller empty ones to oxygen atoms [9]](image-url)
The twelve manganese ions are coupled by strong antiferromagnetic interactions through overlap of electron orbitals via the oxygen atoms (superexchange interactions). As a result, the Mn12-ac molecule can be represented by two sub-ensembles of spins: one contains eight parallel spins each with \( S = 2 \) and, therefore a net spin of 16; the other sub-ensemble contains four parallel spins with \( S = 3/2 \) and a net spin of 6. The net spins of the two sub-ensembles are antiparallel, so the total spin of the molecule is 10. The corresponding magnetic moment is \( \mu = g \mu_B S \approx 20 \mu_B \).

Each cluster occupies a volume of about 1 nm\(^3\), with molecules of water and acetate separating the clusters from one another. As a result, the clusters occupy only about 5% of the total volume of the molecular crystal. The large distance between neighbouring molecules prevents any exchange interaction and allows only weak dipolar interactions.

### 3.3 Properties of Mn12-ac

The major breakthrough in studying Mn12-ac occurred in 1993 when it was reported that the relaxation time of the magnetization of Mn12-ac at low temperatures follows an exponential law.

\[
\tau = \tau_0 \exp\left(\frac{\Delta}{k_B T}\right)
\]

In the range 2 – 15 K, the parameters used to fit the Arrhenius type dependence of the relaxation time of the magnetization, \( \tau \), are: \( \tau_0 = 2.1 \times 10^{-7} \) s and \( \Delta/k_B = 62 \) K. We can see this dependence on Fig. 4.

![Figure 4: Temperature dependence of the logarithm of the relaxation time of the magnetization of Mn12-ac [9]](image)

The curve has been obtained by ac susceptibility measurements at higher temperatures, and by directly measuring the time dependence of the magnetization at lower temperatures [6]. The horizontal lines correspond to 1 second (1s), 1 hour (1h) and
1 year (1y). As we can see this means that at 2K the relaxation time becomes of the order of a few months. At the lowest temperature at which reliable relaxation measurements were performed, 1.5K, the relaxation time was estimated to be of the order of 50 years. As a result, we can define a ‘blocking temperature’, $T_B$, above which the rate of spin reversal is much faster than the measurement timescale. Mn12-ac has a blocking temperature of about 3 K.

The magnetic hysteresis loop of the Mn12-ac was also measured, during the investigation of the magnetization. It was shown that magnetic hysteresis has a characteristic stepped curve, which is not usually observed in classical magnets and is the signature of quantum effects. A typical plot of the magnetic hysteresis of the Mn12-ac is shown on the next page in Fig. 5.

![Figure 5: Magnetic hysteresis curve for single crystals of Mn12-ac][9]

The flat regions of the curve monitor fields at which the relaxation is very slow, while the steps correspond to fields at which comparatively faster relaxation occurs. The field of the steps are to a good approximation equally spaced.

The explanation of the magnetization curve of Mn12-ac crystals is based upon the structure of the spin energy levels of Mn12 molecules. The Mn12 cluster has a tetragonal symmetry. In the magnetic field $H_z$, applied along the tetragonal axis, it is described by the Hamiltonian [10]:

$$\mathcal{H} = -DS_z^2 - AS_z^4 - g\mu_B S_z H_z + \mathcal{H}_T,$$

(5)

where $S = 10$, anisotropy $D/k_B \approx 0.55$ K, the fourth-order longitudinal anisotropy $A/k_B \approx 1.2 \times 10^{-3}$ K, $g \approx 1.94$, and $\mathcal{H}_T$ contains small symmetry-breaking terms that do not commute with $S_z$ and as we will show later are responsible for the tunnelling.

The eigenvalues of Hamiltonian written in Eq. 5 are

$$E_m = -Dm^2 - Am^4 - g\mu_B H_z m$$

(6)

Let us recall that we are working with $S = 10$ spin ground state of the Mn12-ac molecule.
If we neglect $H_T$, then in a zero field, the ground state of the cluster is doubly degenerated. The dependence of the energy of the Mn12-ac on the magnetic quantum number $m$ at $H_z = 0$ is shown by the inverted parabola in figure 5. The two energy minima $m = \pm 10$ correspond to the spin pointing up or down along the crystal $z$ axis. They are separated by the magnetic anisotropy barrier $U = 62$ K i.e. the same barrier which determines $\tau$. At low temperature the molecules will be in the lowest lying $m = \pm 10$ state. The transition between negative and positive $m$ occur due to the thermal activation over the anisotropy barrier (upward arrows in Fig. 6) or quantum tunnelling (horizontal arrows in Fig. 6).

Let us now apply the external magnetic field along the positive crystal $z$ direction. In this case the negative $m$ levels shift up while the positive $m$ levels shift down in energy (Fig. 7b). The trivial algebra of Eq. 5 yields that the $m$ and $m'$ eigenvalues of $S_z$ come to resonance at:

$$H_z = H_{mm'} = -(m + m') \frac{D}{g\mu_B} \left[ 1 + \frac{A}{D} (m^2 + m'^2) \right],$$

(7)

At $H_z = H_{mm'}$ the transitions are combinations of thermal activation and quantum tunnelling. Thus for $H_z = H_{mm'}$ the anisotropy barrier is effectively reduced by tunnelling and the magnetic relaxation towards the direction of the field is faster then at $H_z \neq H_{mm'}$. 

Figure 6: Thermally assisted spin tunnelling in spin-10 molecular magnets
Figure 7: Schematic diagram of double-well potential: (a) in the absence of an external magnetic field, and (b) in the presence of a magnetic field applied in the positive $z$ direction for step $N = 3$ ($N = |m + m'|$) \[10\].

In Fig. 7 (b) the solid arrows indicate thermally assisted tunnelling and the dotted line denotes tunnelling from the ground state of the metastable potential well. Due to the presence of the small fourth order term, $AS_z^4$, in the Hamiltonian, different pairs $(m, m')$ of energy levels cross at slightly different magnetic fields. Thus, as indicated in the figure, the pair $(-7, 4)$ comes into resonance at a lower magnetic field than the pair $(-10, 7)$.

### 3.3.1 Origin of the tunnel splitting

In order to have tunnel splitting it is necessary that the pairs of $\pm m$ levels are actually split by some suitable transverse field. As I have already said the last term $\mathcal{H}_T$ in the Eq. 5 represents transverse interactions. Some of the larger terms in $\mathcal{H}_T$ are given in Eq. 8:

$$\mathcal{H}_T = g \mu_B H_x S_x + E \left( S_x^2 - S_y^2 \right) + B \left( S_x^4 + S_y^4 \right)$$ \(8\)

The transverse magnetic field $H_x$ and the other two operators mix together the $m$ wavefunctions and this facilitates tunnelling of the magnetization. More exactly, the second anisotropic term only mixes states differing in $m$ by $\pm 2$, and the third term is responsible for the mixing of the states differing in $m$ by $\pm 4$. 

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3.4 Magnetic relaxation in Mn12-ac

At the beginning of the previous chapter I have mentioned that relaxation of the magnetization follows the Arrhenius law (see Eq. 4). Since the understanding of this is not trivial at all, I will explain the theory behind it.

At first I must correct myself, because the relaxation time of the magnetization does not exactly follow an exponential law. In different experiments it has been discovered that relaxation time has a characteristic minima as a function of applied magnetic field $H$. This implies that magnetic relaxation does not depend only on activated relaxation process but also on field tuned resonant tunnelling between two excited states. We can see this on Fig. 8.

![Figure 8: The variation of the relaxation time of the magnetization as a function of applied field [11].](image)

The relaxation time of the magnetization was measured at 1.9 K. Initially the crystal is cooled in a field of 5 T. The field is then reduced rapidly to the desired value and kept fixed while the relaxation of the magnetization is monitored. The minima seen in the figure occur at the same values of applied field as the steps in the hysteresis curve shown in Fig. 5. The arrows are located at the fields corresponding to the level crossings. The straight line is the classical prediction, the other line is fit to data and the points represent experimental data. The equation which describes such behaviour of relaxation time can be written as:

$$\frac{1}{\tau} = \frac{1}{\tau_{Ar}} + \frac{1}{\tau_T}$$

(9)

Where $\tau_{Ar}$ is relaxation time obtained from Arrhenius law (thermally activated processes), and the term with $\tau_T$ represents the tunnelling effects.
3.4.1 Thermally activated relaxation

There are two usual mechanisms by which magnetic relaxation occurs. These are spin-spin interactions and spin-phonon interactions. In the case of Mn12-ac, spin-spin relaxation should be irrelevant, at least at low temperatures $k_B T \leq \Delta$. Thus, the relaxation of the magnetic moment should be mainly due to spin-lattice interactions. These can be subdivided into two kinds: relaxation due to the modulation of the dipole interaction between Mn spins, and relaxation due to the modulation of the crystal field. In the case of Mn12-ac, the crystal field effect may be expected to be much larger than the dipole mechanism.

The spin-phonon Hamiltonian can be obtained by treating the spin-orbit interaction within second-order perturbation theory. It is, therefore, quadratic in the spin operators. The allowed transitions from a spin state $|m\rangle$ of a given molecule are the spin states $|m+1\rangle$, $|m-1\rangle$, $|m+2\rangle$ or $|m-2\rangle$. However, for the sake of simplicity, a single coupling constant will be assumed, and only transitions from $|m\rangle$ to $|m+1\rangle$ or to $|m-1\rangle$ will be considered.

The spin relaxation process is thus the following: at the beginning, all the molecules are in the $|s\rangle$ state (due to the effect of the magnetic field). The molecules which go to the $|s-1\rangle$ state have to climb first to the state $|s-1\rangle$, then to $|s-2\rangle$, etc., until they reach the top of the potential barrier at $|0\rangle$, and then climb down to $|s-\rangle$. This process is a generalisation of what is known in paramagnetic resonance as an Orbach process. In the usual Orbach process, there is just one high-energy excited state. In the present case there is a cascade of $(2s + 1) - 2 = 19$ intermediate states.

In order to extend Orbach’s calculation to the case of a cascade, it is first necessary to calculate the relaxation rate $\gamma^q_m$ from a state $|m\rangle$ to a state $|q\rangle$. This can be done through the standard golden rule of perturbation theory. The result involves the matrix element $V_{mq}$ of the spin-phonon interaction, the phonon velocity $c$, the specific mass $\rho$ and of course the energy difference $\epsilon_m - \epsilon_q = D (m^2 - q^2)$. One obtains [12]

$$\gamma^q_m = \frac{3}{2 \pi \hbar^4 \rho c^5} \left( \epsilon_q - \epsilon_m \right)^3 \frac{1}{\exp \left[ \beta (\epsilon_q - \epsilon_m) \right] - 1}, \left( \epsilon_q > \epsilon_m \right),$$

and, in agreement with detailed balance:

$$\gamma^q_m = \frac{3}{2 \pi \hbar^4 \rho c^5} \left( \epsilon_m - \epsilon_q \right)^3 \frac{1}{1 - \exp \left[ \beta (\epsilon_m - \epsilon_q) \right]}, \left( \epsilon_q < \epsilon_m \right).$$

Since second-order perturbation theory is assumed to hold, $V_{mq}$ is zero unless $q$ is equal to $m+1$ or $m-1$, in agreement with the selection rule mentioned above.

The second step of the calculation is the solution of the following set of master equations:

$$dp_m(t)/dt = \gamma^m_{m+1} p_{m+1}(t) + \gamma^m_{m-1} p_{m-1}(t) - \gamma^{m+1}_m p_{m+1}(t) - \gamma^{m-1}_m p_m(t),$$

where $p_m(t)$ is the population of molecules in spin state $|m\rangle$. 

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These equations can be solved at low temperatures \((k_B T \ll \Delta)\) when the left side is small, and in the stationary case \(dp_m(t)/dt = 0\). At the end we obtain the expression for Arrhenius relaxation time

\[
\tau = \frac{1}{2} \sum_{q=0}^{2s-1} \exp\left[\beta \left( e_{s-q} - e_s \right) \right].
\]  

(13)

At low temperatures, it is a reasonable approximation to keep only the largest terms \(q = s\) and \(q = s - 1\). In this case the result for \(\tau\) is \([12]\)

\[
\tau = 2 \frac{\exp\left[\beta (e_0 - e_s)\right]}{\gamma_0^{-1}}.
\]  

(14)

### 3.4.2 Tunnelling

The tunnelling rate from various initial states \(m\) is proportional to the product of two factors, the probability for the initial state to be occupied and the tunnelling rate from that initial state. The first of these decreases exponentially with energy according to the Boltzmann distribution, being proportional to \(\exp[-E_m/k_B T]\), where \(E_m\) is the energy of the \(m\)-level. Thus, at zero applied field, the occupation probability for the \(m = 0\) state is lower than the probability for the \(m = \pm S\) state by a factor \(\exp[-DS^2/k_B T]\). This factor is equal to \(\exp[-22] \sim 3 \times 10^{-10}\) for Mn12-ac at 3 K. However, the height and the width of the energy barrier both decrease as the energy of the initial state is increased, thereby increasing the tunnelling rate.

The end result is that the thermally assisted tunnelling rate in Mn12-ac is a maximum for the \(m = \pm 3\) levels in the absence of an applied field. In general, for Mn12-ac it is only possible to observe tunnelling for level crossings that are close to the top of the energy barrier. However, the introduction of a transverse field increases the tunnelling rate, and it is thought that a transverse field of 6 T would allow ground state tunnelling, that is tunnelling between the \(m = -10\) and \(m = 10\) levels, to be observed.

### 4. Perspectives

#### 4.1 Other SMM

Leaving the interesting sea of Mn12 derivatives afforded new types of molecules. The first one was a cluster comprising eight iron(III) ions, \([\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]\)\(\text{Br}_8\) (tacn = 1, 4, 7-triazacyclononane), Fe8, which by chance has a ground state \([9]\).

This compound was found to have a smaller zero field splitting of the ground state compared to Mn12-ac, and a lower symmetry. The smaller zero field splitting gives rise to a comparably faster magnetic relaxation. The absence of the symmetry determines a sizable transverse anisotropy in the \(xy\) plane, thus making the tunnel mechanism more efficient. In fact it is possible to reach the pure tunnelling regime below 300 mK where the relaxation time becomes independent of temperature \([9]\).
A third category of molecules has attracted much attention in the last few years, namely clusters comprising four manganese ions. A particularly interesting example is provided by \([\text{Mn}_4\text{O}_7\text{Cl}_4(\text{O}_2\text{CET})_3(\text{py})_3] \), Mn4 [13]. The four manganese ions are at the vertices of a distorted tetrahedron. Three of them are manganese(III) and the fourth is a manganese(IV). The ground state is \(S = 9/2\) due to dominant antiferromagnetic coupling between the trivalent and the tetravalent ions. Pairs of clusters are at relatively short distance from each other, and they are connected through a frame of hydrogen bonds. Mn4 shows a SMM behaviour, and the hysteresis loops show the same stepped behaviour as discussed above. These clusters show borderline properties between those of large magnetic clusters and antiferromagnetic rings, which are also intensively investigated for quantum effects.

There are also some other magnetic molecules with different number of transitional metal ions (\(\text{Mn}_{18}, \text{Mn}_{30}, \text{Ni}_{12}, \text{Fe}_{10}, \ldots\)), but they all have lower anisotropy barriers and faster magnetic relaxation.

### 4.2 Further developments

The field of molecular nanomagnetism is still in its infancy. The advantage of molecular clusters, compared to all 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 make them interesting object to be addressed individually. If we assume that molecular spin cluster could serve as a computer element to store information, then allowing for a distance of 5 nm between
neighbouring spins, a disc with an area of 100 cm$^2$ could hold a staggering 50 000 gigabytes of spin clusters. Presumably the states $m = \pm S$ would be used to store classical bit. In today’s hard disks where around 1µm of disk is used to store one bit, this means that a storage density is around 200 GB per 100 cm$^2$. At 1,5 K, the relaxation time of Mn12-ac is long enough to be used as a computer element, but the problem of refrigeration would have to be solved. Even bigger problem is the problem of reading and writing the bits. 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 large clusters, which will be investigated for a large number of different properties, which can make them appealing for biocompatibility (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.

5. Conclusion

In this seminar we have learned that there are molecules which behave like magnets. The first one discovered was the Mn12-ac. Their most important property is the slow relaxation of magnetization at low temperatures. The relaxation time is in the order of months at temperature 2 K, and even more at lower temperatures. Because of this they are interesting for use as a computer element.

Magnetization can change its direction by overcoming an energy barrier. As we have seen this can happen by two different processes. First one is thermally activated process, where the molecules magnetization has to ‘climb’ over the energy barrier to change its direction. The relaxation time for this process is described by exponential law. I have also explained the theory behind this behaviour. The second process is quantum tunnelling. Resonant quantum tunnel can occur when pairs of levels are degenerated. Under these conditions the two states may be admixed, determining a small splitting, which may be called the tunnel splitting. Under these conditions comparatively fast relaxation occurs. A non-zero magnetic field mismatches the energies of the $+ m$ and $- m$ level, destroying the condition for tunnel relaxation, thus increasing the relaxation time. The conditions for degenerated levels occur again when the magnetic field reaches the appropriate value. This was the first time that evidence of quantum tunnelling in mesoscopic magnets was achieved.

At the end I have shown some other single molecule magnets, and describe their properties. Also I have listed same future developments in the field of molecular nanomagnets.
References