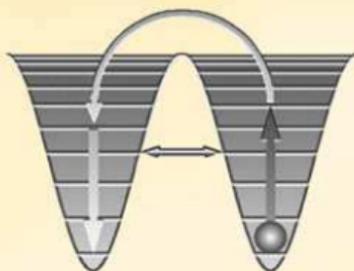
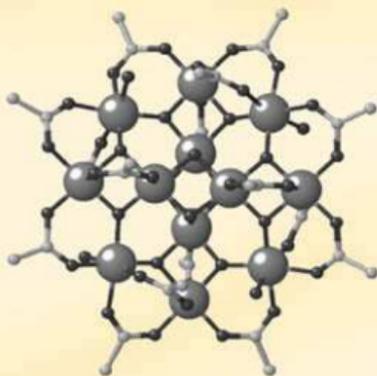


MESOSCOPIC PHYSICS AND NANOTECHNOLOGY

Molecular Nanomagnets

DANTE GATTESCHI
ROBERTA SESSOLI
JACQUES VILLAIN



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Molecular Nanomagnets

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MOLECULAR NANOMAGNETS

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PREFACE

Magnetism has been known to humans for millennia, and for millennia interpretations of the nature of this elusive force capable of moving inert bodies have been produced. An early example is provided by Plinius, who in *Naturalis Historia* wrote: ‘Quid ferri duritia pugnacius? Pedes ei importuit et mores. Trahitur namque magnete lapide, domitrixque illa rerum omnia materia ad inane nescio quid currit atque, ut propius venit, adsilit, tenetur amplexuque haeret.’ Plinius expresses his surprise for the fact that iron, a typical example of hard matter, is irresistibly attracted by lodestone until they embrace. One and a half millennium later, G.B. Porta in his book *Natural Magick* in 1589 similarly wrote ‘iron is drawn by the Loadstone, as a bride after the bridegroom, to be embraced; and the iron is so desirous to join with it as her husband, ...’. Magnetism was understood as a soul of inert matter which transformed it into something like a living organism and expressions like animal magnetism and organic magnetism gradually became popular, especially among charlatans. It was in the nineteenth and twentieth centuries that the nature of magnetism was finally understood, but the magnetic materials were still structurally based on metals or oxides. Finally towards the end of the twentieth century the first examples of magnets based on organic matter were discovered and a new research field, which is commonly defined as molecular magnetism, was opened.

A particularly appealing area in molecular magnetism is that of molecules which show a slow relaxation of the magnetization at low temperature, behaving as tiny magnets and thus known also as single-molecule magnets. These were discovered at the end of the twentieth century and immediately attracted much interest for their relevance to fundamental phenomena, like the coexistence of quantum and classical phenomena and for the opportunities of developing new types of magnetic materials.

The present book is particularly devoted to these single-molecule magnets although more general aspects of molecular nanomagnetism are also addressed. This research field is rapidly expanding and requires the cooperation of chemists, for the challenge of designing and synthesizing new examples of magnetic molecules with tailor-made properties, and of physicists, who can experimentally measure the properties and work out the theoretical models required for their interpretation.

Many research articles, reviews, and book chapters dealing with molecular nanomagnetism have recently appeared but a book covering the different aspects of this new domain was lacking. It was also felt that a field where the chemical and physical expertise is so intimately mixed could be tackled only by a joint effort of people with different backgrounds. The book is in fact written by the chemists

pioneers in this field and by a theorist who has been one of the protagonists of its development. The book is explicitly addressed to an audience of chemists and physicists aiming to use a language suitable for the two communities.

Establishing a common language is certainly a very difficult task. The authors tried to be helpful to the other researchers, especially new-comers, by taking advantage of their reciprocal ignorance in the complementary field. The chapters of the book have been tested in this way, starting with a draft version which was returned full of question marks which showed that what is obvious for one person may be completely obscure for another. A trial and error approach progressively diminished the number of question marks in subsequent versions of the manuscript. The present text has been released when the question marks were acceptably few in the various chapters. The appendix section is fairly large because it was felt appropriate to leave the more demanding mathematical passages available for the interested reader, keeping technicalities to a minimum in the main text.

A further important improvement of the text has been achieved by the careful reading of the different sections by some patient and friendly colleagues who accepted of being the first test of the approach of the book. We thank Giuseppe Amoretti, Pierre Averbuch, Steve Blundell, Andrea Cornia, Pierre Dalmas de Reautier, Julio Fernández, Anna Fort, Andrew Kent, Alessandro Lascialfari, Achim Müller, Wolfgang Wernsdorfer, and Richard Winpenny for the many improvements they have provided to us. Of course all the errors and obscure passages that remain have to be attributed to the authors. We are indebted to our closer collaborators and our families who demonstrated great patience when finding us often occupied with the writing of this manuscript. We also wish to thank the many colleagues who kindly permitted the reproduction of their graphic material.

Dante Gatteschi
Roberta Sessoli
Firenze, July 2005
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Grenoble, July 2005

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INTRODUCTION

Molecular magnetic materials have been added to the library of magnetism only at the end of the twentieth century through the concerted action of chemists and physicists. Before this, all the known magnets were based on metallic and ionic lattices, ranging from magnetite, the first magnet discovered by man, to iron. The interest in functional molecular materials was not limited to magnetism but rather arose from the discovery that purely organic compounds could be electrical conductors, and even superconductors (J erome and Schulz 2002). This prompted much research, because it was immediately clear that organic conductors could open up new technological applications, taking advantage of low cost and the possibility of tuning the properties using chemical techniques. With an obvious extension, the possibility of organic magnets was taken into consideration. After some false starts at the beginning of the 1990s, Kinoshita and co-workers (Tamura *et al.* 1991) in Japan reported the first evidence of a purely organic ferromagnet, based on a nitronyl nitroxide, whose structure is sketched in Fig. 1.1.

Organic radicals, i.e. systems with at least one unpaired electron, are in general unstable, but the nitroxides, which have an unpaired electron essentially localized in a NO group, are relatively stable, and have been widely used as spin probes and spin labels (Berliner and Reuben 1981). An early example of the investigation of ferromagnetic interactions involving organic radicals was provided by Veyret and Blaise (1973). Magnetic ordering was observed (Saint Paul and Veyret 1973)

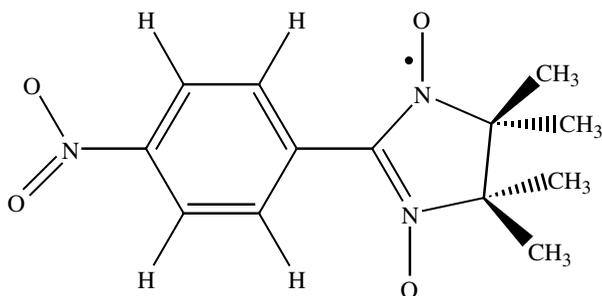


FIG. 1.1. Sketch of the molecular structure of the para-nitrophenyl nitronyl nitroxide, NITpNO₂Ph.

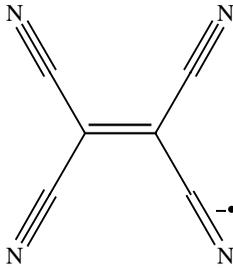


FIG. 1.2. Sketch of the structure of the TCNE^- radical. All the CN groups are equivalent.

but the material at a deeper investigation revealed to undergo a metamagnetic transition (Chouteau and Veyret-Jeandey 1981). Nitronyl nitroxides, like NITpNO_2Ph shown in Fig. 1.1, are a variation on the nitroxide theme, containing two equivalent NO groups in a five-membered ring with one unpaired electron delocalized on the two NO groups. The equivalence of the NO groups in Fig. 1.1 can be verified by writing the symmetric formula in which the double bond and the unpaired electron in the five-membered ring are moved to the symmetric counterpart.

NITpNO_2Ph is ferromagnetically ordered only below 0.6 K; nevertheless it was important because it showed that it is indeed possible to have a permanent magnet in which the magnetic orbitals, i.e. those containing the unpaired electrons, are s and p in nature, rather than the d and f orbitals involved in classical magnets. Currently the purely organic magnet with the highest critical temperature is a sulphur-based radical which orders as a weak ferromagnet below 35 K (Palacio *et al.* 1997).

Before NITpNO_2Ph some other examples of molecular ferro- and ferrimagnets had been reported, based on molecular lattices comprising various transition metal ions and also transition metal ion-organic radicals pairs (Miller *et al.* 1987; Kahn *et al.* 1988; Caneschi *et al.* 1989). In this way, a high-temperature ferrimagnet was obtained, using vanadium ions attached to the radical anions of tetracyanoethylene, TCNE^- sketched in Fig. 1.2 (Manriquez *et al.* 1991). The structure is not known because $\text{V}(\text{TCNE})_2$ is highly insoluble and no single crystals suitable for crystallographic analysis were obtained. However the compound orders above room temperature. The ferrimagnetic order arises from the antiferromagnetic coupling between the $S = 3/2$ of V^{2+} and the $S = 1/2$ of the TCNE^- radicals.

Another room-temperature ferrimagnet is a Prussian blue type compound comprising chromium(III)¹ and vanadium(II) and vanadium(III) ions, of formula $[\text{V}(\text{II})_{0.42}\text{V}(\text{III})_{0.58}(\text{Cr}(\text{CN})_6)_{0.86}]2\text{H}_2\text{O}$ (Ferlay *et al.* 1995).¹

¹ We will use in the following different notations for the formal charge of the metal ions, namely: chromium(III), Cr^{3+} , Cr^{III} . The three must be considered to be equivalent.

Beyond providing some new magnetically ordered systems, molecular magnetism provided several new types of low-dimensional magnetic materials, which attracted the interest of a growing number of physicists, looking for new types of magnetic materials. For instance, materials which provided evidence for the so-called Haldane conjecture (Haldane 1983) are molecular in nature; Kagome-type lattices were obtained (Awaga *et al.* 1994; Wada *et al.* 1997); various types of one-dimensional ferro-, antiferro- and ferrimagnets were obtained, also using unusual constituent spins (Lascialfari *et al.* 2003).

In fact starting from the 1980s there was a marked shift of interest in the field of magnetism of molecular systems, which can be summarized as the transition from magnetochemistry to molecular magnetism. Magnetochemistry is essentially the use of magnetic techniques for obtaining structural information on simple paramagnetic systems, and it is a branch of chemistry which uses physical measurements (Carlin 1986). Molecular magnetism, on the other hand, is an interdisciplinary field, where chemists design and synthesize materials of increasing complexity based on a feedback interaction with physicists who develop sophisticated experimental measurements to model the novel properties associated with molecular materials (Kahn 1993). If one wants to fix a starting date for molecular magnetism the best candidate seems to be the NATO Advanced Study Institute, ASI, which was held in Castiglione della Pescaia in Italy in 1983 (Willett *et al.* 1983). The title of the ASI, 'Structural-magnetic correlations in exchange coupled systems', reflects the interest of the chemist organizers for understanding the conditions under which pairs of transition metal ions could give rise to ferromagnetic interactions. Looking at the list of participants it is clear that there was a blend of chemists and physicists, many of whom met for the first time. A common language started to be developed and useful collaborations were established for the first time. The proceedings of that ASI have been intensively referenced, and have been the textbook for the first generation of scientists active in molecular magnetism.

Important as they have been, the efforts in designing and synthesizing bulk magnets starting from molecules always meet the difficulty that molecules are not easy to organize in a three-dimensional net of strong magnetic interactions. This can be rather easily done with ions or metals, where the building blocks are spherical, while it is often far from being obvious with molecular building blocks, which are in general of low symmetry. This is one of the main reasons why a comparatively large number of low-dimensional materials have been obtained by using molecular building blocks.

However, this difficulty may turn out to be an advantage if the target is changed from three-dimensional magnets to low-dimensional and, in particular, zero-dimensional magnets. Indeed the interest in finite-size magnetic particles had developed in the 1980s as a consequence of the growing interest in the so-called nanoscience. It was realized that nanosize objects can be particularly interesting because matter organized on this scale has enough complexity to give rise to new types of properties, and yet it is not too complex and can be

investigated in depth in much detail. The interest in nanoscience (and, in perspective, for nanotechnology) spans all the traditional disciplines. In condensed matter physics the first steps were perhaps made in the field of conductors and semiconductors, as a result of the impetus on the miniaturization processes associated with more efficient computers. One of the challenges is the realization of objects of size so small that they give rise to the coexistence of classical and quantum properties. The most interesting results were in the field of quantum dots and quantum wires (Bimberg *et al.* 1999), which correspond to objects whose size is in the nanometre range in three or two directions, respectively. Progress was made possible by the development of experimental techniques, which allowed ‘seeing’ and investigating the properties of particles of a few nanometres. Among them a particular relevant place was kept by scanning probe microscopy techniques, like atomic force microscopy, scanning tunnel microscopy, etc. (Bai 2000).

Magnetism could not be an exception, and one of the relevant themes was the possibility of observing quantum tunnelling effects in mesoscopic matter. A scheme, showing the size effects in the magnetization dynamics and hysteresis loop going from multidomain magnetic particles to molecular clusters, has been extracted from an interesting review (Wernsdorfer 2001) and is given in Fig. 1.3.

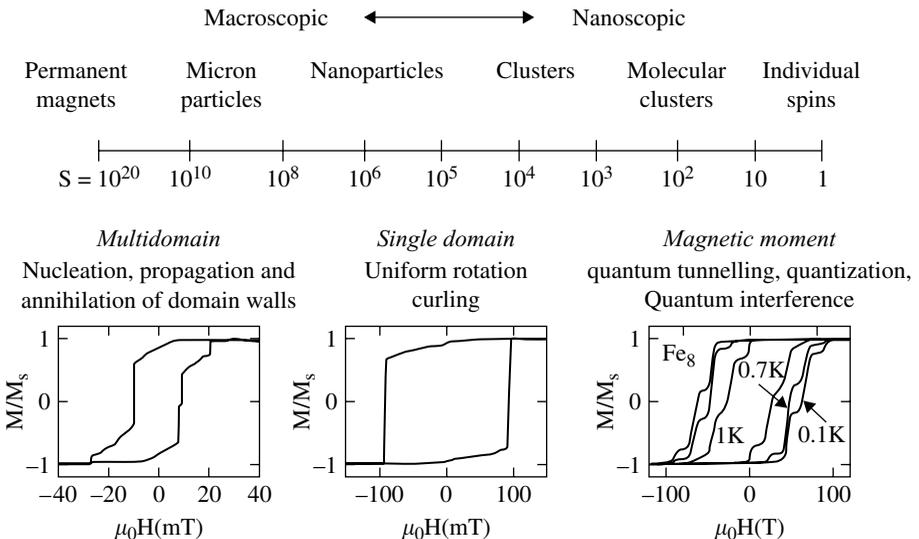


FIG. 1.3. The transition from macroscopic to nanoscopic magnets. From Wernsdorfer (2001). The hysteresis loops are typical examples of magnetization reversal via nucleation, propagation and annihilation of domain walls (left), via uniform rotation (middle), and quantum tunnelling (right). Reprinted with permission of John Wiley & Sons.

At the macroscopic limit the particles contain at least billions of individual spins, which are coupled in such a way that the individual moments will respond all together to external stimuli. The magnetic energy is minimized by forming domains, regions in space within which all the individual moments are parallel (antiparallel) to each other. The orientation of the moments of the domains will be random in such a way that in the absence of an external magnetic field the magnetization of the sample is zero. The transition from a domain to the neighbouring one will occur through a region where the local magnetic moments are rapidly varying, called the Bloch walls (Morrish 1966). The width of the Bloch walls, d , depends on the exchange coupling constant J , which tends to keep the spins ordered and to make the walls as large as possible, in order to minimize the effort needed to change the orientation of the moments, and on the magnetic anisotropy, which tends to minimize the Bloch walls to reduce the probability of high-energy orientations. Obviously the width of the domain walls depends on the nature of the magnetic material.

When the sample is magnetized all the individual moments will eventually be parallel to each other and the magnetization reaches its saturation value. If the field is decreased the formation of domains will not be reversible in such a way that the magnetization at zero field will not be zero, like in the non-magnetized case. The finite value of the magnetization in zero field is called the remnant magnetization. In order to demagnetize the sample it is necessary to go to a negative field, which is called the coercitive field. This value is used in order to classify the bulk magnets: a small value of the coercitive field is typical of soft magnets, while in hard magnets the coercitive field is large. The M/H plot, shown in Fig. 1.3 on the left, shows a hysteresis loop, which tells us that the value of the magnetization of the sample depends on its history. This is the basis of the use of magnets for storing information.

On reducing the size of the magnetic particles a limit is reached when the radius of the particle is small compared to the Bloch wall depth. Energetically the process of domain wall formation is no longer economical and the particle goes single domain.

By further reducing the size of the particles, another effect sets in (Néel 1949). The magnetic anisotropy of the sample, A , depends on the size of the particle:

$$A = KV \tag{1.1}$$

where V is the volume of the particle and K is the anisotropy constant of the material. Let us suppose that the anisotropy of the magnetization is of the Ising type, i.e. the stable orientation of the magnetic moment of the particle is parallel to a given direction z . The energy of the system as a function of the orientation of the magnetic moment is pictorially shown in Fig. 1.4.

The bottom of the left well corresponds to magnetization down, the bottom of the right well to magnetization up, and the top to the magnetization at 90° from the easy axis. On reducing the size of the sample eventually the barrier for the reorientation of the magnetization will become comparable to the thermal

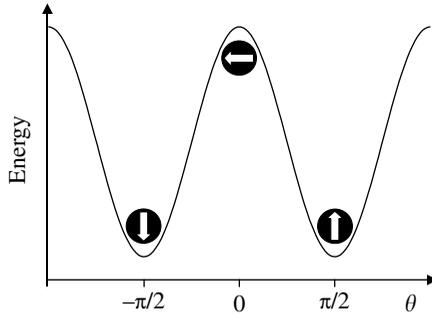


FIG. 1.4. Energy of an Ising (easy axis) type magnet as a function of the angle of the magnetization from the easy axis.

energy. If the sample is prepared with the magnetization up (right well) some of the particles will have enough energy to jump over the barrier and reverse their magnetization. If the particles are given enough time, half of them will be in the left and half in the right well at equilibrium because the two minima have the same energy. The system will no longer be magnetized in zero magnetic field, like a paramagnet. If an external field is applied then one of the two wells will lower its energy and the other will increase it. The two wells will have different populations and the system behaves like a paramagnet, but since the response to the external perturbation comes from all the individual magnetic centres, it will be large. These kinds of particles are called *superparamagnets*, and they find some interesting application, like in magnetic drug delivery, in magnetic separation of cells, and as a contrast agent for magnetic resonance imaging (Pankhurst *et al.* 2003).

An important feature of the superparamagnet is that the observation of either static or dynamic magnetic behaviour depends on the time-scale of the experiment used for investigating it. For instance, using an ac magnetic susceptibility measurement with a field oscillating at $\nu = 100$ Hz, static behaviour, with a blocked magnetization, will be observed if the characteristic time required for the particles to go over the barrier is longer than $\tau = (2\pi\nu)^{-1}$, while dynamic behaviour is observed for shorter τ . The so-called blocking temperature corresponds to the temperature at which the relaxation time of the magnetization equals the characteristic time of the experiment.

The characteristic time for the reorientation of the magnetization can be easily calculated assuming that it occurs through a thermally activated process. This gives rise to an exponential dependence on the energy barrier with so-called Arrhenius behaviour, as observed in many other classes of thermally activated physical and chemical processes:

$$\tau = \tau_0 \exp \frac{KV}{k_B T}. \quad (1.2)$$

This behaviour is typical of a classical system. In principle, when the size of the magnetic particles reduces, it may be possible to invert the magnetization also through the quantum tunnel effect (Leggett 1995). This effect should show up at low temperature, where it should provide the most efficient path for magnetic relaxation only if the wavefunctions of the left and of the right well have some overlap. The quest for quantum effects in magnetic nanoparticles is certainly one of the goals of this book.

The size of the particles needed to observe superparamagnetic behaviour ranges from 2–3 to 20–30 nm, depending on the nature of the material. Magnetic nanoparticles are obtained in many different ways, ranging from mechanical grinding to sol–gel techniques (Sugimoto 2000). An original procedure uses naturally occurring materials like ferritin, the ubiquitous iron storage protein. Iron is needed in the metabolism of living organisms, and it must be stored in some place in order to use when it is needed. Nature chose ferritin to do this job in animals, plants, fungi, and bacteria. Man has an average of 3–4 g iron and ca. 30 mg per day are exchanged in plasma. Structurally ferritin comprises a proteic shell, apoferritin, and a mineral core, of approximate composition FeOOH . The size of the internal core is ca. 7 nm, giving rise to superparamagnetic behaviour in the iron oxide particles, which can contain up to ca. 4000 metal ions (St. Pierre *et al.* 1989).

An interesting feature is that it is possible to substitute the iron oxide core with other magnetic oxides, like magnetite, taking advantage of the proteic shell for limiting the size of the magnetic particles (Wong *et al.* 1998). Indeed ferritin was used in one of the early attempts to observe quantum phenomena in mesoscopic magnets, but only conflicting evidence was obtained (Gider *et al.* 1995; Tejada *et al.* 1997). The problem is that the observation of quantum phenomena is made difficult by the fact that either the experiments are performed on individual particles, or, if an assembly of them is used, they must be absolutely monodisperse. Monodisperse means a collection of identical particles, because quantum phenomena scale exponentially with the size of the particles, and it would be impossible to unequivocally observe quantum phenomena in polydisperse assemblies.

Definite improvements have been made recently in the techniques to obtain monodisperse assemblies of magnetic particles. In some cases it has been possible to obtain identical particles that have been ‘crystallized’ (Redl *et al.* 2003; Sun and Murray 1999). In fact if spherical particles all identical to each other are put together they will try to occupy space in the most efficient way, giving rise to a close packed array exactly as atoms do in crystals.

An alternative to using magnetic nanoparticles, i.e. of reducing the size of bulk magnets in a sort of top-down approach, is that of using a molecular approach in a bottom-up approach (Gatteschi *et al.* 1994). The idea is that of synthesizing molecules containing an increasing number of magnetic centres. In the ideal process one would like to be able to add one magnetic centre at a time, starting from one and going up to say a few thousand magnetic centres. The theoretical