Studies of molecular antiferromagnetic spin clusters and development of magnetic imaging of surfaces

Alberto Ghirri

Relatore: Prof. Marco Affronte

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**Contents**

I  Introduction  

1  Introduction  

  1.1  Molecular nanomagnets  

  1.1.1  Antiferromagnetic spin clusters  

  1.1.2  Heisenberg AF spin segments  

  1.1.3  AF molecular rings for quantum computation  

  1.1.4  Prussian blue analogs  

  1.1.5  Molecular magnets at surface  

  1.2  Scanning Hall Probe Microscopy (SHPM)  

2  Experimental methods and theoretical background  

  2.1  Low temperature set-up  

  2.2  Bulk measurements techniques  

    2.2.1  $ac$-$dc$ magnetometry  

    2.2.2  Calorimetry  

    2.2.3  Torque magnetometry  

  2.3  Scanning Probe Microscopy (SPM)  

    2.3.1  Low temperature $x$, $y$, and $z$ movement  

    2.3.2  Scanning Tunneling Microscopy (STM)  

    2.3.3  Scanning Hall Probe Microscopy (SHPM)  

  2.4  Focused Ion Beam (FIB)  

II  Results  

3  Antiferromagnetic rings with substitution
## CONTENTS

3.1 Heterometallic Cr$_7$M rings ................................................. 59  
3.1.1 Synthesis ................................................................. 59  
3.1.2 Magnetic characterization ............................................. 62  
3.1.3 Conclusions .............................................................. 68  

4 Elementary excitations in antiferromagnetic Heisenberg spin segments. .................................................. 69  
4.1 Cr-based AF spin segments ................................................. 70  
4.1.1 Experimental details ................................................... 70  
4.1.2 Results ................................................................. 73  
4.1.3 Discussion .............................................................. 78  
4.1.4 Conclusions .............................................................. 83  
4.2 Cu twins linked by Cr-based segments .................................. 84  

5 Antiferromagnetic molecular rings for quantum computation ................................................................. 89  
5.1 Cr$_7$Ni as effective two-level system. .................................. 89  
5.1.1 Magnetic characterization ............................................. 89  
5.1.2 Discussion .............................................................. 92  
5.1.3 Conclusions .............................................................. 97  
5.2 A class of two-levels systems: the Cr$_9$Ni ring ..................... 98  
5.3 Entanglement on linked Cr$_7$Ni complexes .......................... 101  

6 SHPM imaging of magnetic domains ........................................... 109  
6.1 Domain branching in ferrite crystals .................................. 109  
6.1.1 Domain branching ................................................... 109  
6.1.2 Experiments ............................................................ 110  
6.1.3 Results ................................................................. 111  
6.1.4 Discussion .............................................................. 116  
6.1.5 Conclusions .............................................................. 117  

7 Prussian blue analogs nanoparticles at surface .......................... 119  
7.1 Magnetic properties of PBA nanoparticles ........................... 119  
7.2 PBA nanoparticles at surface ............................................ 122  
7.2.1 Selective grafting by FIB-direct lithography ..................... 122  
7.2.2 SHPM magnetic imaging ............................................. 125
7.2.3 Conclusions ........................................ 131

III Conclusions ........................................ 133

8 Conclusions ........................................ 135

Bibliography .......................................... 138

Curriculum vitae ...................................... 150

List of publications .................................. 154
Part I

Introduction
Chapter 1

Introduction

In the last years materials and phenomena at the nanoscale have received an increasingly interest as testified by the fact that the terms Nanoscience and Nanotechnology are nowadays of common usage. The interest on these fields arises both because of the fascinating features of the nanoworld and because the Nanoscience promises to transform the present technology. Unusual phenomena happen when the classical world meets the quantum one: the aim of Nanoscience is to understand such an event and possibly to lead to new applications. This motivation, which is supported by the possibility given by the modern scientific instrumentation to attain the resolution at nanometer scale, is pressed by the current technology, for which the continuous miniaturization of the electronic components claims for nano-devices in the near future. In addition, the difficult task to organize and control materials at the nanoscale is a strong stimulus for the whole research to develop new tools and techniques for such a purpose.

This thesis reports some experimental work on molecular magnets and the development of Scanning Hall Probe Microscopy (SHPM) for magnetic imaging. Molecular nanomagnets are objects that allow, to some extent, to tailor the magnetic properties starting from the very bottom, i.e. the molecular level. This name comes from the fact that the magnetic behavior can be described by considering a unique magnetic moment for each nanoparticle. In the case of single-molecule magnet, at sufficiently low temperature, the molecular magnetic moment is essentially defined by the spin ground state. Molecular magnets
are intrinsically quantum systems and they have actually shown, since the begin-
ingning of the ’90s, intriguing quantum phenomena, such as the tunnelling of
magnetization and quantum interference (Berry’s phase). The attention of many
researchers is now focalized to exploit the functionalities of these nanomagnets
in view of ultra high density memories or quantum information processing. Both
applications require the positioning of a single molecular magnets at surface: this
topic is therefore investigated by many research groups dealing with magnetism,
surface science and chemistry. Several results have already been obtained for
the deposition of single layers, but a complete magnetic characterization is still
lacking because of the requirements in terms of low-temperature, magnetic field
and spatial resolution. This issue motivates us to develop SHPM for such an
application.

The outline of this thesis is the following: Chapter 1 briefly reviews the sub-
jects of interest. Chapter 2 describes the experimental set-up and techniques.
Chapter 3, 4 and 5 are devoted to the study of bulk molecular magnets: Chapter 3
deals with the study the series of Cr-based antiferromagnetic rings with substitu-
tion, Chapter 4 discusses the spin excitations in finite segments and Chapter 5
handles the implementation of quantum computation in antiferromagnetic spin
clusters. The Scanning Hall probe microscopy is introduced in Chapter 6, where
the technique tested by investigating the magnetic domain pattern at ferrite sur-
face. Chapter 7, lastly, deals with the subject of molecular magnets at surfaces,
discussing the fabrication and magnetic characterization of single layers of Prus-
sian blue nanoparticles.
1.1 Molecular nanomagnets

Nanomagnetism is a subfield of nanoscience dealing with magnetic structures of nanometer dimensions. New and promising applications could arise from this branch of science, spintronic for instance is a new kind of electronic where the charge property of the electron is combined with the spin [1,2].

In this context, molecular magnetism represents the ultimate tool to create nano-objects with the tailored magnetic characteristics [3,4]. Synthetic chemistry has developed an extraordinary capability to produce new metal-organic compounds. A molecular magnet is a cluster, typically with size $\sim 1$ nm, where a finite number of magnetic centers (transition-metal, rare-earth ions, or even organic radicals) are strongly coupled by organic bridges [5] that work as paths for the exchange interaction. In most of the cases, the intra-cluster magnetic interactions are stronger than those among clusters: the bearing of the molecule is therefore unrelated to the environment.

This bottom-up approach allows therefore to construct magnetic materials starting from the molecular level. The molecules are typically packed in ordered crystals with macroscopic size. One nice thing of single-molecule magnet behavior is that the properties observed in bulk crystals essentially reflect those of the single molecule. Measurement techniques on bulk sample have thus access to microscopic properties (considering the ensemble average), probing quantum effects. The tunneling of the magnetization, is certainly the most popular one. This phenomenon takes place in molecules with anisotropy barrier and high spin, such as Mn$_{12}$-ac [6–8] and Fe$_8$ [9] and it consists in the tunneling of the magnetization through the anisotropy barrier.

1.1.1 Antiferromagnetic spin clusters

Mn$_{12}$-ac has been the most studied system because of its high spin $S = 10$, that arises by the interplay of ferromagnetic and antiferromagnetic interaction among the manganese atoms of the cluster, and its high anisotropy barrier. Another interesting class of magnetic molecules is constituted by antiferromagnetic (AF) rings: ferric wheels, e.g. Fe$_6$ [10], Fe$_{10}$ [11,12], Fe$_{12}$ [13,14], Fe$_{18}$ [15] (with Fe$^{3+}$ ($s = 5/2$)), Cr-based molecular rings like Cr$_8$ [16] and Cr$_{10}$ [17] (comprising
Cr\(^{3+}\) (s = 3/2)) and, V-based rings like V\(_8\) and V\(_{10}\) [18] (V\(^{3+}\) (s = 1)) were synthesized. Cr\(_8\) (Fig. 1.1(a)) represents a paradigmatic case for this category in which carboxylate and fluoride bridges between the eight Cr\(^{3+}\) (s = 3/2) ions give rise to a planar and regular octahedron [19].

The common feature of these systems is the small number n of paramagnetic ions and nearest neighbor Heisenberg exchange interaction:

\[
\mathcal{H}_{ex} = \sum_{i=1}^{n-1} J_i \mathbf{s}_i \cdot \mathbf{s}_{i+1},
\]

(1.1)

where \(J_i > 0\) is the AF exchange constant. The coupling between spin centers leads to a characteristic ground state total spin \(S = \sum_{i=1}^{n} s_i = 0\), due to the exact compensation between the spin centers within the ring (Fig. 1.1(b)), and general features of the energy spectra. The diagonalization of the Hamiltonian 1.1 (Ref. [20–22]), shows that the energy multiplets are typically structured in three bands (Fig. 1.2): the lowest one, named L-band, is a rotational band that follows
Figure 1.2: Energy spectrum of Cr₈ ring versus total spin quantum number $S$ ($J_{Cr-Cr}/k_B=16.9$ K). Arrows indicate the transitions probabilities measured by inelastic neutron scattering and their labeling. Values at states give exact energies in units of $|J|$. (Further details are given in Ref. [22])

the Landé rule:

$$E(S) = \frac{2J}{n} S(S + 1). \quad (1.2)$$

These excited states are characterized by the rotation of the oppositely oriented total spins of each sublattice. The second group, named $E$-band, is generated by higher energy excitations, which appears with one sublattice spin decreased by one in analogy with spin waves. The remaining states form a quasi-continuum [19,21].

In molecular arrays or crystals of AF rings, the long-range interactions are in most of the cases negligible both because no super-exchange paths between clusters are available, and because the small total spin of the clusters give rise to minimal inter-cluster dipolar interactions. The magnetic anisotropy arises from crystal field and dipolar intra-cluster interactions. In comparison to the exchange interaction of Eq. 1.1, their effect is small but finite. The crystal field anisotropy $D_1$ can be expressed as the sum of one axial term and one rhombic term. The resulting Hamiltonian therefore reads:

$$\mathcal{H}_{cf} = \sum_{i=1}^{n} \mathbf{s}_i \cdot \mathbf{D}_i \cdot \mathbf{s}_i = \sum_{i=1}^{n} d_i [s^2_{z,i} - s_i(s_i + 1)/3] + \sum_{i=1}^{n} e_i [s^2_{x,i} - s^2_{y,i}], \quad (1.3)$$
1. Introduction

where \( \hat{z} \) is the axis orthogonal to the ring plane. Because of the cyclic symmetry, the axial anisotropy constant \( (d_i) \) is always greater than the rhombic one \( (e_i) \), so these wheels can be considered in good approximation uniaxial systems [19]. The dipolar interaction is given by:

\[
H_{\text{dip}} = \sum_{i>j=1}^{n} \mathbf{s}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{s}_j = - \sum_{i>j=1}^{n} \frac{\mu_0 \mu_B^2}{4\pi r_{ij}^3} \left( 3(g_i \mathbf{s}_i \cdot \mathbf{r}_{ij})(g_j \mathbf{s}_j \cdot \mathbf{r}_{ij}) - (g_i \mathbf{s}_i \cdot g_j \mathbf{s}_j) \right),
\]

(1.4)

being \( r_{ij} \) the distance between the spins, \( g_i \) the gyromagnetic factor and \( \mu_B \) the Bohr magneton. The full Hamiltonian therefore reads:

\[
H = H_{\text{ex}} + H_{\text{cf}} + H_{\text{dip}} + H_{\text{Zeeman}} = \sum_{i=1}^{n-1} J_i \mathbf{s}_i \cdot \mathbf{s}_{i+1} + \sum_{i=1}^{n} \mathbf{s}_i \cdot \mathbf{D}_i \cdot \mathbf{s}_i + \sum_{i>j=1}^{n} \mathbf{s}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{s}_j + \mu_B \sum_{i=1}^{n} g_i \mathbf{H} \cdot \mathbf{s}_i,
\]

(1.5)

where the last term accounts for the Zeeman effect due to the external magnetic field \( \mathbf{H} \). The anisotropic part of \( H \) does not commute with the squared total spin operator \( S^2 \) thus it mixes subspaces corresponding to different values of the total spin \( (S\text{-mixing}) \). Nevertheless, the energy spectrum at \( H = 0 \) is well approximated by \( S \)-defined multiplets because the entity of the anisotropic interactions is small.

The pattern of the energy levels can be calculated by the diagonalization of the Hamiltonian Eq. 1.5. This is a demanding computational task, because Eq. 1.5 can no longer be independently diagonalized within each \( (2S + 1) \)-dimensional block because of its reduced symmetry. The complete Hamiltonian matrix, which for \( \text{Cr}_8 \) has dimensions \( 65536 \times 65536 \), ought to be considered. For such a purpose, an efficient solution scheme based on the irreducible tensor operator formalism was developed in Ref. [23], which has the peculiarity to maintain the simple total-spin description even in the presence of mixing between different multiplets.

The eigenstates of \( H \) are used to calculate the physical observables, which are then compared to the experimental data in order to determine the parameters of Eq. 1.5. The pattern of the energy levels can be calculated as well; the results for \( \text{Cr}_8 \) are shown the result is shown in Fig. 1.3, where the low-lying states of \( \text{Cr}_8 \) as a function of \( H \) are considered. Accordingly to Fig. 1.2, the ground state \( S = 0 \) is followed by the \( S = 1 \) and \( S = 2 \) excited multiplets, which are split at zero-field by the anisotropic terms of \( H \). The Zeeman effect describes the evolution of the
Molecular nanomagnets

Figure 1.3: Energy levels of Cr$_8$ calculated by the spin Hamiltonian Eq. 1.5 with the parameters of Ref. [19]. The angle between $\mathbf{H}$ and $\hat{z}$ is $\theta = 65^\circ$. (From Ref. [24])

Energy levels as a function of $H$. Ground state crossing between $S = 0$ and $S = 1$, and $S = 1$ and $S = 2$, is expected for $H_{C1} = 6.9$ T and $H_{C2} = 14$ T respectively.

1.1.2 Heisenberg AF spin segments

Infinite spin chains have attracted interest of physicists for long time since they are model systems in which different types of excitations can be created depending, for instance, on the character of the exchange interaction, anisotropy, or the spin. A remarkable example is the Haldane prediction: a gap opens in the energy spectrum when the spin value of the magnetic centers is integer but not in the case of half-integer spin chains [25, 26].

In the last decades the study of the excitations of Heisenberg spin chain has received a large interest from both the theoretical and experimental points of view [27]. More recently the attention was drawn to finite spin chains or "segments". For short enough chains, the low lying energy levels can be directly evaluated by diagonalizing the spin Hamiltonian and the finite size leads to a discrete energy spectrum. Examples of spin segments are spin chains broken by impurities or engineered atomic structures [28]. Broken AF rings, as Cr$_7$Cd [29] and Cr$_7$Zn [30], can be regarded as an alternative molecular route to obtain well
ordered spin segments.

For low spin values, these systems have purely quantum-mechanical character (Fig. 1.4) and one interesting issue is the localization of excitations in finite spin chains. It is known that edge states in both integer and half-integer chains arise from exchange interactions [32–36], whilst localized states [37,38] can be observed when non-linear effects are significant. Spin segments, or finite spin chains, may also have special boundary conditions imposed at the terminations that may strongly influence the character of excitations [39].

Being the intermediate step between (semi-)infinite Heisenberg chains and closed rings, molecular segments open a new promising route to perform targeted studies of finite spin chains. With respect to statistical doping of infinite chains, this bottom-up approach to synthesize spin segments has the obvious advantage that there is no size dispersion. Besides, the possibilities of chemical control over length, doping, spin values are remarkable and still in part unexplored.
1.1.3 AF molecular rings for quantum computation

Quantum computation indicates a new way of computation which deploys the coherent evolution of a quantum system as calculation procedure, the final state of the quantum system is the result of the calculation. Such a method, whose basic idea arises by the parallelism between the algebra describing quantum phenomena and some computational problems, has huge calculation potentialities.

There is a general agreement to identify the basic requirements for the quantum system with the DiVincenzo criteria [40, 41]:

1. Identification of a well-defined qubit: the quantum states of the candidate system must be well described and well separated from other possible states not directly involved in computation.

2. Initialization: a reliable experimental procedure must be defined in order to set the qubit in a well defined initial state.

3. Accurate quantum gate operations: exploiting the parallelism between computation and quantum mechanics, a quantum gate operation corresponds to the motion (coherent time evolution) of the system from an initial quantum state to a final state. These dynamics must be described by the Schrödinger equation.

4. Low decoherence: gate operations occur in finite time and to be reliable the coherent time evolution should not be perturbed by other agents. For solid state quantum devices this is one of the most delicate aspects since the device is, by definition, embedded in the environment made of nuclear and electronic spins, lattice vibrations, charge carriers and electromagnetic radiation. For a reliable qubit, it would be required the gate rate to be $10^4$ times more rapid than the time at which the system loses coherence. In practice this is quite hard to achieve with solid state systems but should be taken as reference goal.

5. Readout: a method to read the final state should be defined and experimentally realized. It should be noted that quantum information resides in the superposition of the basis set of states.
1. Introduction

Figure 1.5: The scheme of Meier, Levy and Loss. The qubit is realized by a spin cluster where the internal spins $s_i$ are coupled by $J$. Two-qubit operations are achieved using a switchable inter-cluster exchange interaction with $J_e < J$. (From Ref. [31])

Figure 1.6: Proposed scheme for the implementation of two-qubit gate with non-local field and permanent coupling between sites. The scheme explicitly refers to AF wheels. (a) Schematics of the lowest energy levels of the AB system with and without (right-hand and left-hand sides, respectively) the effective intercluster coupling. (b) Sketch of the linear array of rings ABAB... , with asymmetric couplings between each two neighboring units. (c) Intracluster ordering of the electron spins characterizing the ground-state doublet of a prototypical AF wheel. Possible intercluster molecular links (solid lines), can locally couple spin $i$ of ring A with $j$ and $j + 1$ of B. (d) The excited state $|b_1\rangle$ of B lacks the above antiparallel arrangement of the adjacent spins. (From Ref. [44])
Molecular nanomagnets

Since a decade, great attention is devoted to electron spins localized in low-dimensional semiconductor heterostructures. Both ferromagnetic [42] and antiferromagnetic [31, 43] molecular spin cluster were proposed as alternative implementations. At low temperature, these systems show discrete energy levels where to observe coherent dynamics and perform quantum gates. The chemical synthesis allows both to tailor their electronic properties and to produce identical arrays of clusters. Several methods are under development for the positioning of molecular magnets on surfaces (see Section 1.1.5).

Because of their relatively simple energy spectrum, AF spin clusters are actually considered the most promising molecular systems for encoding qubits. In the approach proposed in Ref. [31, 43], Meier, Levy and Loss consider a spin clusters with dominant antiferromagnetic internal exchange coupling and total ground state \( S = 1/2 \) (Fig. 1.5). Quantum gates are generated by pulsed magnetic fields (one-qubit gates) and a switchable inter-cluster exchange interaction (two-qubit gates), that is used to create entangled states.

The need of magnetic field locally resolved at the cluster size (\( \sim 1 \) nm) is actually a challenging experimental requirement. Troiani et al. (Ref. [44]) have developed a scheme suitable for permanently coupled AF rings that, exploiting the excited states, avoids the need of local magnetic fields (Fig. 1.6). Referring to a total ground state \( S = 1/2 \) wheel as qubit, they assumed that a permanent link exists between two molecules, hereafter named A and B. The ground state of the isolated A and B systems is described by antiparallel alignment of spins. For sake of simplicity, they further assume the link to be preferentially coupled to one spin of A, while it interacts with the two spins of B, e.g., via local interactions to the neighboring spins \( i \) and \( i + 1 \). In this case, the overall effective interaction is proportional to \( \langle s_i \rangle + \langle s_{i+1} \rangle \), and thus vanishes when B is in its ground state (being \( \langle s_i \rangle \sim \langle s_{i+1} \rangle \)), whilst it becomes finite if B is driven to an excited states (say \( \mid 2 \rangle \)) lacking such antiparallel alignment of the neighbouring spins [44].

A first attempt to create entanglement of molecular spin states was reported by Wernsdorfer et al. in Ref. [45], where a \([\text{Mn}_4]_2\) molecular dimer was investigated. This complex, namely \([\text{Mn}_4\text{O}_3\text{Cl}_4(\text{O}_2\text{CET})_3(\text{py})_3]_2\), was obtained by supramolecular linkage of the \text{Mn}_4\ molecules by means of H-bonds (Fig. 1.7). Both the six C-H···Cl pathways and the Cl···Cl approach, cause the overlap-
Figure 1.7: The structure of the $[\text{Mn}_4\text{O}_3\text{Cl}_4(\text{O}_2\text{CCH}_3)_3(\text{py})_3]_2$ dimer, denoted $[\text{Mn}_4]_2$. The small circles are hydrogen atoms. The dashed lines are C-H···Cl hydrogen bonds and the dotted line is the close Cl···Cl approach. Brown, oxygen; green, manganese; red, chlorine; blue, nitrogen; py, pyridine. (From Ref. [45])
Figure 1.8: Sketch of a bimetallic Prussian blue analog. At the vertices, black spheres represent Cr$^{3+}$ with spin $s = 3/2$, whereas lighter-colored spheres represent Ni$^{2+}$ with spin $s = 1$. Depicted as well are the Cs atoms at the interstitial sites. The lattice parameter is $a = 10.50$ Å. (From Ref. [49])

The overlap of the Cl-py and Cl-Cl orbitals of the two molecules, that establishes sizable AF superexchange bonding ($J/k_B = 0.1$ K). The energy spectrum results from the antiferromagnetic coupling between the $S = 9/2$ total spin of the isolated Mn$_4$, which give rise to entangled $S = 0$ ground state.

### 1.1.4 Prussian blue analogs

Prussian blue analogs (PBA) are extended molecular systems for which long-range magnetic ordering up to room temperature has been reported [46, 47]. Many derivatives were synthesized, where exchange coupling between divalent and trivalent metals is achieved through cyano-bridges. The structure of bimetallic (NiCr)-PBA, nominally CsNi$^{2+}$[Cr$^{3+}$(CN)$_6$]·(H$_2$O), is depicted in Fig. 1.8; Ni$^{2+}$ and Cr$^{3+}$ ions are positioned at the vertex of the cubic lattice, while half of the tetrahedral interstitial sites are occupied by cesium atoms to preserve charge neutrality [48].

The (NiCr)-PBA derivative undergoes a transition to a long-range ferromag-
netic ordered state between 70 and 90 K, depending on the concentration of Cs and H$_2$O [48]. Fig. 1.9 shows the real component $\chi(T)$ of the ac-susceptibility (Ref. [49]), the abrupt change of $\chi(T)$ at $T_C \simeq 90$ K is ascribed to the transition to the ferromagnetically ordered state. In fact, the value of 73.5 emu mol$^{-1}$ reached by $\chi(T)$ at $T_C$ is close to that expected for an isotropic ferromagnetic (NiCr)-PBA sample at the maximum, provided that demagnetizing factor is considered. Below $T = 70$ K, $\chi(T)$-vs-$T$ is linear. The fit to the Curie-Weiss law provides the Curie constant $C = 3.2$ emu K mol$^{-1}$ and the Weiss constant $\theta = 118$ K, in agreement with the observed ferromagnetic ordering. The value of $C$ is reasonably well accounted for by the expected value of randomly oriented spins that amounts to 3.1 emu K mol$^{-1}$, assuming $g = -2.2$ for Ni$^{2+}$ and $g = 2$ for Cr$^{3+}$ ions. The dc-magnetization $M$-vs-$H$ taken at $T = 5$ K, is almost saturated at $H \simeq 0.25$ T. Noteworthy is the fact that the saturation magnetization amounts to 4.6 $\mu_B$ (Fig. 1.9), which is less than the expected value 5.2 $\mu_B$ for Ni$^{2+}$ and Cr$^{3+}$ spins aligned parallel. This observation evidences the canting between the
magnetization of the Ni$^{2+}$ and Cr$^{3+}$ sublattices, which can be forced parallel to the field direction only at $H \gg 7$ T.

### 1.1.5 Molecular magnets at surface

Basic requirement for the exploitation of functionalities of molecule-based materials is their selective deposition on a substrate. Forthcoming applications, such as quantum computation or ultra high density data storage, require the addressing of a single molecule, which may take place using a nanofabricated substrate or a scanning device.

For such a purpose, the first important issue is the design of appropriate derivatives and the implementation of procedures to graft them onto suitable substrate surfaces. In the last years, a great attention was devoted to the deposition of single-layers of Mn$_{12}$ derivatives. Several procedures were developed, in particular deposition via exposure to organic solvent vapors [50], direct attachment on gold using sulfur-functionalized derivatives [51], attachment on gold or silicon.
surfaces previously functionalized with carboxylate groups via a ligand-exchange reaction [52] and a two-step procedure in which polycationic Mn_{12}-bet are deposited onto a gold surface previously functionalized with an anionic self-assembled monolayer (SAM) [53]. Other important achievements were also obtained in grafting other molecular systems like 2-D self-assembled terbium-phtalocyanine [54] and molecular Cr_7Ni wheels [55] (see Fig. 1.10).

Another important issue is the positioning of the molecules onto the surface. Both chemical and physical approaches were developed to organize these clusters in a controlled way: micro-contact printing [56–58], photolithography [59], self-assembling by water droplets templates [60], local oxidation nanolithography [61] and deposition on FIB-patterned substrates [62] were reported.

Particular attention is now devoted to procedures that combine top-down (lithography) with bottom-up (functionalization of either substrate or molecule) methods. These techniques indeed allow the selective deposition on user-defined portions of the surface, avoiding the need of additional lift-off steps with chemicals. Fig. 1.11 shows the procedure followed by Martínez et al. in Ref. [61]. The substrate is firstly functionalized with proper amino-terminated SAM [53], and then patterned by means of local oxidation nanolithography, which is performed using an atomic force microscope (Fig. 1.11(a–b)). After the steps (b) and (c), the grafting of Mn_{12}-bet occurs on the patterned regions only, firstly because of the attractive electrostatic interaction of the molecules with the trapped charges generated during the local oxidation process, and secondly because of the expected repulsive interaction between the amino-terminated SAM and the positively charged polycationic derivative.
Figure 1.11: Schematic procedure of the nanoscale positioning of Mn$_{12}$-bet on SiO$_2$ substrate. (a) Formation of an amino-terminated SAM on a Si(100) surface. (b) Local oxidation of a region of the surface. (c) Deposition of a macroscopic drop containing a solution of polycationic Mn$_{12}$-bet (dark disks). (d) The final result: the molecules on the unpatterned areas are removed rinsing the sample, while polycationic Mn$_{12}$-bet molecules graft on the nano-patterned regions only. (From Ref. [61])

Figure 1.12: Patterns fabricated by using local oxidation nanolithography before and after deposition of SMM. (a) Atomic force microscopy (AFM) image of two parallel stripes. (b) Cross section taken along the line shown in (a). (c) Topographic image of the pattern shown in (a) after the deposition of Mn$_{12}$-bet. The molecules appear as white dots in the image. (d) Topographic image showing a dot of local oxide (diameter 80 nm). (e) Phase-contrast image that reveals the presence of 16 clusters. (From Ref. [61])
1. Introduction

Figure 1.13: The value of $B$ in vacuum is equal to $H$. Close to a paramagnetic material an additional contribution to $B$ arise by the magnetization $M$ of the sample. Note that the lines of flux are deviated by the magnetic region.

1.2 Scanning Hall Probe Microscopy (SHPM)

Although integral techniques still have relevance, the experimental investigation of the surface magnetism needs suitable tools for local measurements and surface imaging. Historically, the development of these techniques begun for the study of magnetic domains (see Ref. [63] for a complete review).

The magnetization of a material is locally described by the vector field of magnetic polarization $M(r)$, being $r$ the position vector inside the material [64]. This quantity is related to the magnetic field $H$ and the magnetic flux density $B$ by the relation:

$$B = H + 4\pi M.$$  \hspace{1cm} (1.6)

In a paramagnetic material, $H$ induces the magnetization $M$ (Fig.1.13). $B$ can be considered as the vector field that includes the effect of both $H$ and $M$, and it represents the density of magnetic flux $\phi$ through a region $S$, $B = \phi/S$. The intensity of $B$ changes inside and outside the material because of the magnetization of the material. Maxwell’s equation $\nabla \cdot B = 0$ yields:

$$\nabla \cdot H = -4\pi \nabla \cdot M$$  \hspace{1cm} (1.7)

which implies that any divergence of $M(r)$ gives rise to $H$. When the sample has a spontaneous magnetization $M$ and no external field is applied, $B = H$ is
simply the stray field in a region outside the magnetic material and generated by
it (Fig.1.14).

A first classification among the techniques for surface magnetism measure-
ments can be established on the basis of which field, $B$ or $M$, is measured. Bitter microscopy with magnetic colloids [65] and magnetic force microscopy
(MFM) [66] probe the the stray field $B$. Other techniques such as magneto-
optical Kerr-effect (MOKE) [68], scanning electron microscopy with polarization
analysis (SEMPA) [69] and X-ray circular dichroism (XMCD) [70], sense directly
the sample’s magnetization $M$. Noteworthy member of the last class is the spin
polarized scanning tunneling microscopy (SP-STM), which allows to resolve the
surface magnetization signal at the atomic scale [71].

Because of their high resolution, versatility, and to be relatively less expensive
than other techniques at large scale facilities, scanning probes have recently ob-
tain a great interest. These instruments can be properly designed to work in
many environmental conditions, such as high vacuum and low temperature. MFM, for
instance, is the most popular magnetic probe. Likewise atomic force microscopy,
MFM senses the magnetic force between the surface and a ferromagnetic tip [67].
Although it achieves a good lateral spatial resolution (about 10 nm), MFM ac-
tually suffers of some limitations: the magnetic tip can be invasive and it has a
micromagnetic state which is rarely know with any confidence and may change
under applied magnetic field. In addition, the technique maps gradients of the
magnetic force rather than directly the magnetic field.

In order to address some of these problems, several techniques have been de-
veloped which essentially deploy more sophisticated devices as flux sensitive sen-

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Figure 1.14: Schematic of the polarization of a magnetic material.
1. Introduction

Figure 1.15: Left: SHPM images of a single Fe disk (diameter 2 µm) for $T = 80$ K and several $H$. Center and right: OOMMF simulations. (From Ref. [96])
Scanning Hall Probe Microscopy (SHPM)

Scanning Hall Probe Microscopy (SHPM) is a technique that involves the use of Hall probes. SHPM is characterized by its high sensitivity, allowing it to pick up tiny magnetic signals across a wide range of temperatures and magnetic fields. The Hall probe, with sensitivity down to $10^3 \mu_B$, is a key component of this method. Hall magnetometers have found numerous applications, including measurements on single-domain superparamagnets, ferromagnetic particles, superconductors, and micro-crystals of molecular magnets. Hall probes have also been proposed as scanning heads for perpendicular recording, with some technological interest related to the first hard disk using perpendicular media commercialized in 2006.

The main advantage of SHPM is its direct sensitivity to stray field $B$ through the Hall effect, enabling measurement of the local field without sensor-surface interaction. Seminal studies by Chang et al. [86] in 1992 demonstrated the use of a gold-coated SHPM sensor for STM tip positioning and SHPM-STM imaging. More recent developments have extended SHPM applications to non-conducting surfaces. Commercial SHPM sensors exhibit resolution up to $\sim 500$ nm, comparable to MOKE. Nano-sized Hall probes have been developed, potentially improving lateral resolution to $50$ nm.

In the literature, SHPM has been used to study superconducting materials and magnetic domains. Oral et al. [91, 92] used SHPM to investigate the real-time evolution of vortex in superconducting crystals and films. Fukumura et al. [93] studied domain features of layered ferromagnetic crystals, while Neal et al. [94-96] examined domain properties of intermetallic materials, respectively films and microstructures, under varying applied fields.

Neal et al. [96] specifically studied the internal domain configuration of a single Fe disk, grown epitaxially on a GaAs substrate, with a diameter of 2 $\mu$m and thickness of 20 nm. SHPM images were taken with a high...
resolution 200 nm Hall probes. The results (Fig. 1.15) show the evolution of the domain pattern when the magnetic field is applied in the plane of the sample. Micromagnetic calculations, which were performed by OOMMF program [97], show a remarkable agreement with the measured profiles.
Chapter 2

Experimental methods and theoretical background

2.1 Low temperature set-up

Most of the experimental work of my thesis consisted in low-temperature measurements that were performed utilizing the Quantum Design Physical Properties Measurements System (QD-PPMS). Most of the effort was devoted to test and use a low temperature Scanning Probe Microscope (Nanomagnetics Instruments LT-SPM). I used the QD-PPMS cryogenic set-up for both bulk measurement and LT-SPM.

The QD-PPMS allows fine setting of the temperature in the range 0.3 – 400 K. Magnetic field up to 7 T can be applied by means of a superconducting coil. A two-stages pneumatic insulation system, needed for LT-SPM, is utilized to reduce vibrations.

The QD-PPMS set-up is sketched in Fig. 2.1 and it is installed in the low temperature laboratory of University of Modena.

2.2 Bulk measurements techniques

To study the thermodynamic properties of the bulk samples I used ac-dc magnetometry, calorimetry and torque magnetometry. These measurements were
Figure 2.1: Quantum Design PPMS: (a) dewar and controller and (b) schematic view of the probe. The cooling of the sample is achieved filling the cooling annulus with liquid Helium or gas whilst heater and thermometer control the temperature. Magnetic field is applied along the vertical direction.
performed by means of the interchangeable options and programmable data acquisition of QD-PPMS [98].

### 2.2.1 ac–dc magnetometry

#### Theoretical background

In a multilevel magnetic system at the thermal equilibrium, the magnetization is given by:

\[
M = k_B T \frac{\partial \ln Z}{\partial H}
\]  

(2.1)

where \( Z \) is the partition function. For a paramagnetic material the magnetization follows the Brillouin function:

\[
\frac{M}{N_A \mu_B} = gS \left[ \frac{2S + 1}{2S} \coth \left( \frac{2S + 1}{2S} x \right) - \frac{1}{2S} \coth \left( \frac{1}{2S} x \right) \right]
\]  

(2.2)

being \( g \) the gyromagnetic factor, \( S \) the total spin momentum, \( \mu_B = 0.671 \text{T K}^{-1} \) the Bohr magneton, \( k_B = 1.381 \times 10^{-23} \text{ J T}^{-1} \) the Boltzmann constant and

\[
x = \frac{g \mu_B S H}{k_B T}.
\]  

(2.3)

The susceptibility is defined as:

\[
\chi = \frac{\partial M}{\partial H} = k_B T \frac{1}{Z} \frac{\partial Z}{\partial H}.
\]  

(2.4)

that for paramagnet reduces to the well-known Curie law:

\[
\chi = \frac{C}{T},
\]  

(2.5)

where

\[
C = \frac{g^2 \mu_B^2 S(S + 1)}{3k_B}.
\]  

(2.6)

It is often convenient to consider the product \( \chi T = C \), that for paramagnetic materials gives directly \( S \) and \( g \). For instance, being \( g = 2 \) and \( S = 1/2 \), \( \chi T = 0.375 \text{ emu K mol}^{-1} \).

In antiferromagnetic spin clusters, for \( T \) above a few degrees K, the temperature dependencies of the susceptibility \( \chi T \) products are almost completely
determined by the dominant Heisenberg contribution of the Hamiltonian Eq. 1.5. Therefore, $\chi_T$ can be evaluated by using the expression

$$\chi_T = \frac{N A g^2 \mu_B^2}{3k_B} \sum_i S_i(S_i + 1)(2S_i + 1)e^{-\epsilon(S_i)/k_B T}$$

where the sum is over all the spin-multiplets eigenstates ($\epsilon(S_i)$) of the Heisenberg hamiltonian Eq. 1.1. To calculate $M(H)$, anisotropic terms have to be included considering the orientation respect to the magnetic field.

The measurement of the susceptibility can be performed by using the $dc$ or $ac$ methods. For the measurement of static magnetic properties they give the same outcome. For time-dependent phenomena, the $ac$-susceptibility has the useful feature to allow the measurement of both the real, or in-phase component $\chi'$, and the imaginary, or out-of-phase component $\chi''$ of the complex susceptibility, $\chi = \chi' - i\chi''$.

The magnetization resulting from an applied dc-field $H_0$ plus an oscillating field $H_{ac} = he^{i\omega t}$ with frequency $\omega$, is given by:

$$M = M_0 + \chi he^{i(\omega t + \phi)}$$

where the equilibrium magnetization is indicated by $M_0 = \chi H_0$ and $\phi$ is the dephasing between the excitation and the response of the system. Within the linear response approximation [99], the approach of the magnetization $M(t)$ to $M_0$ after a field change is characterized by exponential variation with time:

$$M = M_0(1 - e^{-t/\tau})$$

where $\tau$ is the spin-lattice relaxation time. Both the real and imaginary susceptibilities are frequency dependent, their expression is given by the equations:

$$\chi' = \chi_S + \frac{\chi_T - \chi_S}{1 + \omega^2 \tau^2}$$

and

$$\chi'' = \frac{(\chi_T - \chi_S)\omega \tau}{1 + \omega^2 \tau^2}$$

where $\chi_S = \chi_{\omega \to \infty}$ is the adiabatic susceptibility and $\chi_T = \chi_{\omega \to 0}$ the isothermal susceptibility. Fast relaxation time $\tau \to 0$ gives $\chi' = \chi_T$ and $\chi'' = 0$, finite values of $\chi''$ are thus related to time-dependent phenomena. $\chi''$ is a measure of the
dissipative losses of the magnetic system and it is also relate to the dephasing $\phi$ in Eq. 2.8 [100]. Note that $\chi''$ is maximized at $\omega\tau = 1$, so the relaxation time may be determined from the maximum of the out-of-phase susceptibility measured as a function of $\omega$.

The relaxation time for superparamagnetic particles with uniaxial anisotropy barrier $E_a = KV$, being $K$ the anisotropy constant (of magnetocrystalline or shape origin) and $V$ the volume of the particle, follows the Arrhenius law:

$$\tau = \tau_0 e^{E_a/k_B T} \quad (2.12)$$

that is typical of thermal activated processes. For a superparamagnetic system the factor $\tau_0$ typically ranges between $10^{-8} - 10^{-10}$ s.

**Experimental details**

In this thesis work I performed magnetization and susceptibility measurement by means of QD-PPMS magnetometer, that allows both ac and dc measurements in the temperature range $1.9 - 400$ K. It consists in a set of coils inserted in the main dc superconducting magnet (0 – 7 T) (Fig. 2.2).

dc-measurements are performed by means of the extraction technique. The magnetic field is applied by the dc-superconducting magnet and the sample is
moved by the a servo motor through the detection coils, thus inducing a voltage signal proportional to the magnetic moment.

ac-susceptibility is measured providing an oscillating excitation field with the primary coil, with frequency in the range 1 Hz-10 kHz and typical amplitude 10 Oe. Two secondary coils detect the change in magnetic flux due to the sample that is positioned in one of them. They are arranged in a first order gradiometer configuration (i.e. wounded in counter sense) to reject background signals. A compensation coil is also wounded around the driving coil to reduce environmental noise, avoiding interaction with any material outside the measurement region (chamber walls, magnet core, etc.). Special calibration coils are employed to precisely remove phase shifts coming from the detection apparatus and effectively separate sample signal from instrumentation effects.

Units. Data measured by the QD-PPMS acquisition program are given in units of emu, whereas the susceptibility $\chi$ and the magnetization $M$ are usually expressed as emu mol$^{-1}$ and $\mu_B$/f.u. respectively. The necessary transformations are:

$$\chi (\text{emu mol}^{-1}) = \chi (\text{emu}) \times \frac{\text{molar mass (g mol}^{-1})}{\text{sample mass (g) \cdot excitation field (Oe)}}$$  \hfill (2.13)

$$M(\text{DC}) (\mu_B/\text{f.u.}) = M(\text{emu}) \times \frac{\text{molar mass (g mol}^{-1})}{\text{sample mass (g) \cdot \mu_B \cdot N_A}}$$  \hfill (2.14)

where in c.g.s. units $\mu_B$ and $N_A$ are defined as $9.274 \times 10^{-21}$ erg G$^{-1}$ and $6.022 \times 10^{23}$ mol$^{-1}$, respectively. The unit erg G$^{-1}$ is equivalent to emu.

2.2.2 Calorimetry

Theoretical background

The specific heat $C$ of a given material, that is the heat capacity per unit mass (or mole), is defined as the derivative of its internal energy $U$ with respect to the temperature,

$$C = \frac{\partial U}{\partial T}.$$  \hfill (2.15)

In molecular magnets, the main contribution to $C$ are given by the lattice vibrations $C_{\text{latt}}$ and the magnetic contribution $C_{\text{mag}}$, $C = C_{\text{latt}} + C_{\text{mag}}$. 36
In a perfect crystal, there are $3N$ independent modes of lattice vibration, with $N$ the number of ions in a unit cell. Consequently, since molecule-based materials usually contain hundreds of ions per cell, their specific heats tend to saturate to a huge Dulong and Petit value $3NR$ at high temperatures ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) [101]. Because it grows very fast with temperature, even at $\sim 10$ K the lattice contribution is still predominant, thus masking most of the features of the magnetic contribution $C_{\text{mag}}$. In the quantum theory of solids, the lattice specific heat is related to harmonic vibrations (phonons) of the crystal basis respect to their equilibrium position:

$$C_{\text{latt}} = \sum_{k,s} \frac{\partial}{\partial T} \frac{\hbar \omega_s(k)}{\exp(\beta \hbar \omega_s(k)) - 1}$$  \hspace{1cm} (2.16)

where $\omega_s(k)$ is the frequency of the $s$-th mode of vibration with wavevector $k$. Because of the huge number of independent vibration modes, the details of the spectrum are rather complex and the calculation of $C_{\text{latt}}$ by means of Eq. 2.16 it is not feasible. The usual approximation that is applied considers an idealized simplified crystal with three acoustic branches and $(3N-3)$ optical branches. The three acoustic branches are treated within the Debye model, giving the so-called Debye contribution $C_D$, while the optical modes are described by the Einstein model giving the corresponding $C_E$ contribution, so that $C_{\text{latt}} = C_D + C_E$. The Einstein and Debye contributions are respectively expressed as:

$$C_E = 3 \left( \frac{T}{T_E} \right)^2 \frac{\exp \left( \frac{T}{T_E} \right)}{\left[ \exp \left( \frac{T}{T_E} \right) - 1 \right]^2}$$  \hspace{1cm} (2.17)

where $\epsilon_E = k_B T_E$ is the energy of the optical phonon mode and

$$\frac{C_D}{R} = 9 \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} \frac{xe^x}{(e^x - 1)^2} dx$$  \hspace{1cm} (2.18)

where $\hbar \omega_D = \hbar c k_D = 2\pi k_B \Theta_D$ is the Debye energy for which the characteristic linear dispersion $\omega_D = c k_D$ of the acoustic branch is assumed, with $c$ the velocity of sound. For $T \ll \Theta_D$ (typically $T \leq \Theta_D/50$) the latter equation can be approximated as:

$$\frac{C_D}{R} = 234 \left( \frac{T}{\Theta_D} \right)^3$$  \hspace{1cm} (2.19)
In practice the $T^3$ behaviour is hardly visible in molecular compounds. In the temperature range 0.1-20 K the typical behaviour of the lattice contribution is $C_{\text{latt}} \propto T^{\alpha}$ with $\alpha \sim 2.6 - 3$ and the typical $\Theta_D$ values that one obtains range between 15 and 50 K. These $\Theta_D$ values are much lower than usually found for insulating solids or intermetallic compounds ($\Theta_D$ typically ranges within 150 to 600 K in these cases). Below $T = 10$ K, the lattice contribution $C_{\text{latt}}$ is mainly due to acoustic branches of phonons but low energy optical phonons may contribute as well. Alternative phenomenological expressions to fit $C_D$ are calculated in Ref. [102] by fitting the specific heat of a crystal composed of non-magnetic molecular rings:

$$\frac{C_D}{R} = \frac{234rT^3}{(\Theta_D + \delta T^2)^3}, \quad (2.20)$$

where the parameter $r$ is the number of atoms per molecule and $\Theta_D$ and $\delta$ are determined by least square fitting.

The magnetic contribution $C_{\text{mag}}$ to the specific heat can be calculated by the energy $U_{\text{mag}}$ of magnetic system:

$$U_{\text{mag}} = \sum_i n_i \epsilon_i. \quad (2.21)$$

assuming a canonical Boltzmann distribution describing the population $n_i$ of levels $\epsilon_i$. So, since $C_{\text{mag}} = \partial U_{\text{mag}} / \partial T$, for a two-level system we have the expression of the Schottky anomaly:

$$\frac{C_{\text{mag}}}{R} = \frac{g_0}{g_1} \left( \frac{T_0}{T} \right)^2 \frac{\exp \left( \frac{T_0}{T} \right)}{\left[ 1 + \frac{g_0}{g_1} \exp \left( \frac{T_0}{T} \right) \right]^2} \quad (2.22)$$

where $g_0$ and $g_1$ are the degeneracies of the ground and the first excited state, respectively, and $k_B T_0$ is the energy gap between these two states. If $g_0 = 1$ and $g_1 = 1$ the Schottky anomaly has a characteristic maximum at $T \simeq 0.4 \times T_0$ so the energy gap $k_B T_0$ can be immediately visualized by looking at the temperature at which the anomaly exhibits its maximum. If the magnetic system has many levels $\epsilon_i$ the Schottky expression can be generalized as:

$$\frac{C_{\text{mag}}}{R\beta^2} = \sum_i \epsilon_i^2 \exp (-\beta \epsilon_i) \sum_i \exp (-\beta \epsilon_i) - \left[ \sum_i \epsilon_i \exp (-\beta \epsilon_i) \right]^2 \over \left[ \sum_i \epsilon_i \exp (-\beta \epsilon_i) \right]^2 \quad (2.23)$$
Figure 2.3: Sketch of the calorimeter. The holder, with sample, heater and thermometer is linked to the thermal bath by means of $K_1$.

Figure 2.4: Sketch of the calorimeter. The holder, with heater and thermometer, is linked to the thermal bath by means of $K_1$. The sample is linked to the holder block by means of $K_2$.

This expression is commonly used to describe the magnetic contributions in molecular magnets. In antiferromagnetic spin clusters, $\epsilon_i(H)$ are the eigenvalues of the Hamiltonian (Eq. 1.5).

**Theory of measurement**

With reference to Fig. 2.3, the heat capacity measurement is performed supplying a controlled heat quantity $Q(t)$ by the heater to the sample and the holder block so the response of the system is given in terms of temperature changes $T(t)$. The
2. Experimental methods and theoretical background

Figure 2.5: (a) The QD-PPMS calorimeter. (b) The calorimeter holder hosts thermometer and heater. The link to the thermal bath is realized by four wires. The measurement is performed under high vacuum ($10^{-5}$ Torr) to limit the conductivity toward the thermal bath.

relevant quantity is the total heat capacity $C_{tot} = C + C_{add}$, being $C$ the heat capacity of the sample and $C_{add}$, that stands for *addenda*, the heat capacity of the calorimeter. The latter gives a small but finite contribution to $C_{tot}$ and its value is given by the sum of the heat capacity of the single components of the calorimeter, $C_{add} = C_{holder} + C_{heater} + C_{therm}$, that in first approximation can be assumed in excellent thermal contact. The energy balance of the system can be written:

$$\frac{\partial Q(t)}{\partial t} = K_1(T)(T_1 - T_0) + C_{tot}(T) \frac{\partial T_1(t)}{\partial (t)}$$  \hspace{1cm} (2.24)

where the term on the left is the rate of heat dissipated by the heater, the first term on the right is the heat flowing through $K_1$ from the system to the thermal bath and the second term on the right is the heat used for the temperature variation of the system (sample + addenda). $T_0$ is the fixed temperature of the thermal bath while $T_1(t)$ is the actual temperature of the system (sample + addenda) that is time-dependent.

Since $K_1(T)$ and $C_{tot}(T)$ are functions of $T$, the differential equation 2.24 is in general non-linear. It can be nevertheless linearized assuming that $Q(t)$ is small and it gives limited variations of $T_1$. In this case $K_1(T)$ and $C_{tot}(T)$ can be expanded in power series of $T$ and limited to the lowest order. Different solutions of Eq. 2.24 are possible with a convenient choice of the thermal conductivity $K_1$ and of the time dependence of the heat $Q(t)$ [103]. A particular solution is
obtained when:
\[
\frac{\partial Q}{\partial t} = P \Theta(t - t_0)
\]  
(2.25)
(step like heat signal starting at \( t = t_0 \)) and \( K_1 \) is finite. The solution results therefore:
\[
T_1 - T_0 = \frac{P}{K_1(T)} e^{-\frac{t-t_0}{\tau_1}}
\]  
(2.26)
where \( \tau_1 = C_{tot}/K_1 \) is the relaxation time. \( \tau_1 \) can be obtained fitting the exponential relaxation of \( T_1(t) \) afterwards the pulse \( Q(t) \), while \( K_1 \) can be measured directly, thus allowing to calculate \( C_{tot} \). This method, known as relaxation method, was proposed by Bachmann et al. [104] and it is used by QD-PPMS for automatized heat capacity measurements.

Organic materials have often a bad thermal conductivity, so the approximation of Eq. 2.24 is no longer valid. Fig. 2.4 displays a more realistic model of the calorimeter stage, where a finite \( K_2 \) is considered, that accounts both the physical link between sample and holder block, and the rate of internal equilibrium of the sample. \( K_2 \) establishes an internal relaxation time \( \tau_2 = C/K_2 \). The energy balance is more complicates in this case, and it turns out that, in the limit \( \tau_1 > \tau_2 \), the temperature rise (or decay) following a heat pulse is essentially given by the sum of two exponentials, and the total specific heat can be analytically derived from the fit of the temperature relaxation with good precision, typically 1 or few per cent [105, 106].

For the measurement that I show in Chapter 3-5, the quality factor of the measurement, defined as \( c = (\tau_1 - \tau_2)/\tau_1 \), was \( c \simeq 0.9 \). This value assures \( \tau_1 \gg \tau_2 \), hence a distinguishable behavior of the two exponential components of the temperature relaxation \( T(t) \).

**Experimental details**

The calorimeter is shown in Fig. 2.5: the platform hosts the resistor-heater and thermometer, that provide the heat pulse which gives the temperature displacement. In order to reduce the thermal conductivity toward the thermal bath (the cryostat), the platform is suspended and held by four thin wires and the sample chamber is pumped to high vacuum (10\(^{-5}\) Torr).
The value of $K_2$ can be maximized choosing flat samples with large base. Measurements were performed on powders and single crystals. The former were pressed ($\sim 100\text{Bar}/\Phi5\text{mm}$) to create thin pellets. The sample was glued to the calorimeter with Apiezon N grease.

The QD-PPMS achieves temperature down 0.3 K utilizing an additional Helium-3 refrigerator (Fig. 2.6). The closed-circulation system condenses $^3\text{He}$ in a reservoir linked to the specimen. Down to 0.5 K the reservoir is continuously refilled, whereas the $^3\text{He}$ gas must be completely condensed to achieve 0.3 K, so the base-line temperature is kept no longer than one hour before re-cycling.

**Units.** Data acquired by the PPMS calorimeter are given in units of $\mu\text{J K}^{-1}$. To obtain the molar heat capacity and then normalize the data to the molar gas constant $R$ this simple equation can be used:

$$C/R = C(\mu\text{J K}^{-1}) \times \frac{\text{molar mass(g mol}^{-1})}{\text{sample mass(g)}} \times \frac{10^{-6}}{R(\text{J mol}^{-1} \text{ K}^{-1})}$$

where $R=8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. 

42
2.2.3 Torque magnetometry

Theoretical background

The magnetic anisotropy can be evaluated experimentally by means of the torque magnetometry. A magnetic crystal with magnetization $\mathbf{M}$ that is positioned into a magnetic field $\mathbf{H}$ experiences a torque momentum $\tau = \mathbf{M} \times \mathbf{H}$, per unit of volume. The torque magnetometry allows the measurement of a projection $\tau_y$: this quantity is related to the difference between the magnetic susceptibility $\chi_{xx}$ and $\chi_{yy}$ in the orthogonal directions. In a classical material:

$$\tau_y = \frac{1}{2}(\chi_{xx} - \chi_{zz})H^2 \sin(2\theta)$$

being $\theta$ is the angle between the direction of the magnetic field and the $z$-axis. For a quantum system, $\tau_y$ can be expressed as a function of the average of the spin projection operators:

$$\tau_y = \frac{\partial \mathcal{H}}{\partial \theta} = g\mu_B H (\langle S_z \rangle \sin \theta - \langle S_x \rangle \cos \theta),$$

where $\mathcal{H}$ is the Zeeman term of Eq. 1.5. In the simplest case the anisotropy is uniaxial and $\tau_y \sim H^2 \sin(2\theta)$. The outcome of $\tau_y$ vs $\theta$ for $H$ fixed, is a sinusoid with period $2\theta$. The sign of the anisotropy is directly obtained by the sign of the sinusoid: the anisotropy axis is easy when for a small angle off the easy axis, the torque momentum withstands the twisting. The absolute value gives the amplitude of the magnetic anisotropy.

Experimental details

The Quantum Design torque magnetometer is sketched in Fig. 2.7. It consist of a silicon device with a thin lever suspended by two arms that is free to twist in the direction indicated as $\hat{y}$ [107]. The sample is glued on the lever with a small drop of cryogenic grease (Fig. 2.8). An external motor allows the rotation of the device respect to the direction of magnetic field ($\hat{z}$). The misalignment of $\mathbf{M}$ and $\mathbf{H}$ generates a magnetic torque $\tau$, in particular the component $\tau_y$ induces the twisting of the lever. This effect can be measured in a Wheatstone resistive bridge by means of two piezoresistors positioned on the arms, whose resistance is
2. Experimental methods and theoretical background

Figure 2.7: Schematic of the Quantum Design torque magnetometer. The device works down to $T = 2$ K. A motor allows the position control from $-10^\circ$ to $370^\circ$. It's important noting that the torque sign is opposite to that of the positive sign of rotation by using the QD-PPMS set-up and software.

Figure 2.8: Picture of the QD-PPMS torque magnetometer with a crystal of Cr$_7$Ni positioned on the torque lever.
related to the twisting:
\[ \tau_y \sim \frac{R_1 - R_2}{R_{\text{bridge}}} \]  \hspace{1cm} (2.30)

The torque measurement is calibrated by the magnetic moment generated suppling a current through the coil path stamped on the lever (Fig. 2.7). The instrument works in the temperature range 1.9 – 300 K. Typical size of crystals is \( \sim 1 \text{ mm}^3 \) and mass \( \sim 0.1\text{ mg} \) (Fig. 2.8).

*Units.* Calibrated QD-PPMS torque measurements are given in N m.
2. Experimental methods and theoretical background

Figure 2.9: (a) Nanomagnetics LT-SPM. The right side is the air part, with cable connections to the electronic cabinet. The rod 1 m long holds the low temperature head (panel (b)). (c) Particular of the Hall sensor and holder.

2.3 Scanning Probe Microscopy (SPM)

During my thesis work, I used a commercial microscope (Nanomagnetics Instruments LT-SPM) that allows STM, SHPM and AFM microscopy. The instrument can work as insert for the QD-PPMS cryostat (Fig. 2.9).

2.3.1 Low temperature x, y, and z movement

The LT-SPM includes two piezotubes: the first allows the fine movement driving the x, y and z shift of the sensor and is utilized for the measurement. The second moves the sample and it is used for the coarse sample positioning and approaching. The sample (not depicted in Fig. 2.9) has to be installed on a brass puck, then fixed to a glass cylinder that, in turn, is attached to the coarse piezotube. This sophisticated geometry is studied to implement the inertial sliding method for the coarse movement [108, 109]. With reference to the z approaching, the inertial sliding system is constituted by glass cylinder and brass puck. The glass cylinder is driven by a simple asymmetric sawtooth waveform provided by the coarse piezotube. The piezoelectric extends under an applied voltage. During
the slow ramp of the sawtooth, the sample puck stick to the glass cylinder due to static friction. When the fast ramp of the sawtooth, is reached, the inertia of the slider plates is large enough to overcome static friction, resulting in a net displacement. At each step, the sensor $z$ position is also retracted and slowly approached by the fine piezo (stick-slip method) until a tunneling current is found. A similar technique is also utilized for the coarse $x, y$ movement of the sample. While demanding a very accurate cleaning and smoothness of the slider components in order not to stick the movement at low temperature, the inertial sliding technique has the advantage to allow a very compact design that is suitable for the reduced dimensions of the QD-PPMS sample chamber. Because of the temperature dependence of the piezotubes’ characteristics, the scanning area shrinks down from $56 \times 56 \mu m^2$ at room temperature to $4.5 \times 4.5 \mu m^2$ at $T = 2$ K.

### 2.3.2 Scanning Tunneling Microscopy (STM)

The Scanning Tunneling Microscopy (STM) is a powerful tool which exploits the electron tunneling effect between a metallic tip and a conductive sample to investigate the electronic properties of surfaces [110]. This method, which has been developed by Binnig et al. in 1982 [111], allows very high spatial resolution and nowadays atomic-scale resolution is achieved in many commercial systems.

In a very first approximation, sample and tip when are apart can be regarded as free particle states separated by an energy barrier (Fig. 2.10(a)). The work function $\Phi_1$ and $\Phi_2$, of the two systems gives the height of this barrier (which is generally asymmetric because $\Phi_1 \neq \Phi_2$). The electronic wave functions decay exponentially into it, so when sample and tip are brought sufficiently close together, the electrons can tunnel through, giving rise to an appreciable current $I_T$ (Fig. 2.10(b)), which is related to the density of states of the sample. The shape of the barrier of potential can be modified applying a voltage $V_T$ between sample and tip, allowing the current to flow in both the directions.

Fig. 2.11 shows the working principles of STM. The control unit (CU), by means of the piezotube $P_z$, adjusts the separation between tip and sample in order to keep constant the tunneling current $I_T$. Because of the exponential decay of the electronic current through the barrier, this distance is just few angstrom. The piezotubes $P_x$ and $P_y$, scan the tip on the surface. The STM image is just the
2. Experimental methods and theoretical background

Figure 2.10: Principles of the tunneling effect. The shape of the energy gap and wavefunctions is sketched when sample and tip are (a) separated, and (b) brought close together.

matrix representing the value of the voltage $V_z$ applied to $P_z$ in order to keep $I_T$ constant in each position $x, y$. STM thus investigates the local density of states of the sample, which it is probed by varying $I_T$ and $V_T$ [110]. In first approximation the STM image can be appreciated as the topography of the surface. This interpretation is nevertheless misleading: the presence of flat regions with different conductivity induces variations of the tip height as well as shown in Fig. 2.11.

The tip is the most critical component of the STM apparatus. The ideal tip is a sharp needle that has only one atom at the apex. Because of the exponential decay of the electronic wave functions inside the energy barrier, in such a tip 90% of the current intensity flows through one atom whereas the 99% through the first atomic layer. When this situation is realized, STM achieves the atomic resolution. In practice, the STM tip has a finite radius of curvature that gives rise to lateral broadening (see Fig. 2.11). Furthermore, the atomic structure of the vertex is strongly related to the presence of adsorbates that alter shape and conductivity. Environmental noise from mechanical vibrations or electrical interferences may worsen the experimental conditions and thus reduce the spatial resolution of STM as well.
2.3.3 Scanning Hall Probe Microscopy (SHPM)

The Scanning Hall Probe Microscopy makes use of Hall sensor as magnetometer to locally probe the magnetization of surfaces. The measurement of the magnetic flux is direct and non-invasive since it is based on the Hall effect. The SHPM is constituted also by a STM tip that is utilized to control the position of the sensor [86].

The Hall effect

In 1879 Edwin H. Hall found that in a wire where a current is flowing, a transverse voltage appears when a perpendicular magnetic field is applied (Fig. 2.12). The explanation of this phenomenon can be described in the framework of the Drude model. A current is flowing through the material in the x-direction and a magnetic field $B$ is applied along $z$. The charge carriers undergo a Lorentz force:

$$ F = q(E + v \times B) $$

(2.31)

where $q$ is the charge and $v$ the drift velocity of the carriers [101]. This force deflects the charge carriers toward the negative $y$-direction, generating an elec-
2. Experimental methods and theoretical background

Figure 2.12: (a) The Hall effect. (b) Hall cross-sensor. Two pins are utilized to inject $I$ and the remaining to measure $V_H = R_H I B_z$ (Eq. 2.33).

trostatic potential $E_y$ that prevents for a further accumulation. In stationary conditions, $eE_y = ev_x B_z$. The Hall voltage is thus given by:

$$V_H = w E_y = v_x B_z = \frac{j_x B_z}{ne}$$  \hspace{1cm} (2.32)

where $w$ is the width of the conductor, $j_x$ the current density along $x$ and $n$ the charge carriers density. Since $j = I/wd$ ($d$ is the thickness), the final relation is obtained:

$$V_H = R_H I B_z$$  \hspace{1cm} (2.33)

having defined the Hall coefficient $R_H$ as

$$R_H = \frac{E_y}{j_x B} = \frac{1}{ned}$$  \hspace{1cm} (2.34)

The Hall voltage $V_H$ turns out to be proportional to both the magnetic field and the current and inversely proportional to the carrier density $n$ of the conductor. Thus, the Hall effect can be used to determine $n$ and the sign of charge carriers in a material. The relation:

$$B_z = V_H / R_H I$$  \hspace{1cm} (2.35)

shows that, when $R_H$ is known, a Hall device can be used as magnetometer to evaluate $B_z$ by measuring the Hall voltage $V_H$ (Fig. 2.12). The Hall magnetometer, like SQUID [112], is actually a flux-meter: when positioned close to a magnetized sample, it probes directly the stray field $B^{sf}_z$:

$$V_H = R_H I_H (B_z + B^{sf}_z)$$  \hspace{1cm} (2.36)

which can be evaluated subtracting the linear contribution of $B_z$. 50
Figure 2.13: The Hall probe shows a linear $V_H$ vs $H$ behavior in the field range $-70 \leq H \leq +70$ kOe.

**Sensitivity**

The magnetic sensitivity of a Hall sensor is given by the minimum detectable magnetic field ($B_{min}$). This quantity is related by the ratio between the intensity of the electrical noise that affects the measurement and the Hall signal $V_H$:

$$SNR = \frac{\sqrt{V_{Johnson}^2 + IR_{noise}^2}}{IR_H}.$$  \hspace{1cm} (2.37)

The two major contributions to the noise are: (i) the Johnson intrinsic thermal noise, which arises from the resistance of the device channel $V_{Johnson} = \sqrt{4k_BT R_s \Delta f}$, being $k_B T$, $R_s$ and $\Delta f$ respectively the thermal energy, series resistance of the device and the measurement bandwidth; (ii) the telegraph noise, which acts on the time trace of the Hall signal $IR_{noise}$ [113]. As it can be seen in Equation 2.37, the Johnson noise can be reduced increasing the intensity of the driving current $I$, although above a certain value it is overcome by the resistivity noise. Besides, self heating effects ($I^2R$) impose constraints on the value of $I$. Summing up, there is an optimal, material dependent, value for the driving
current that minimize the noise effects. Both the noise sources of equation 2.37 are weakened by low temperature.

The minimum detectable field $B_{\text{min}}$ is also limited by the extrinsic noise due to current sources, amplifiers and wirings. In LT-SPM, this constitutes the leading contribution. The noise voltage of the hardware is $\approx 1 \, \mu V$ that, considering the gain $10^3$ of the amplifier circuit, gives $B_{\text{min}} \approx 1 \, \text{G}$.

**SHPM sensors**

Commercial Hall probes utilize high mobility semiconductors to achieve high resolution to magnetic flux. The standard choice is InSb for room temperature applications and GaAs/AlGaAs two dimensional electron gas (2DEG) for low temperatures. These materials are chosen for the special combination of low density of charge carriers ($n$) and high mobility ($\mu$). The small value of $n$ give rise to high Hall coefficient since $R_H \propto 1/n$ (Eq. 2.34), while high mobility $\mu$ results in small serial resistance.(Ref. [113]).

I utilized commercial Hall probes (Nanomagnetics Instruments) which are crosses of patterned GaAs heterostructures (Fig. 2.14). They show excellent linear
response to magnetic fields (Fig. 2.13), having Hall coefficient $R_H$ of 0.22 $\Omega$/G at room temperature and 0.27 $\Omega$/G at $T = 2$ K. The active area has width 800 nm. The effective magnetic spatial resolution of the sensor is enhanced by the depletion of carriers at the edges of the channels, and it achieves resolution of $\simeq 500$ nm at $T = 2$ K.

In these SHPM sensors, a corner of the Hall probe is gold coated and utilized as STM tip to control the position and simultaneously acquire STM images [86]. The sensor is depicted in Fig. 2.14. The Hall probe is positioned at 13 $\mu$m from the STM tip. The sample must be tilted of $\alpha \simeq 1^\circ$ in order to prevent the crash of other parts of the sensor: as a consequence, the minimum distance between the Hall probe and the surface (height) is $h = 13 \mu m \times \sin (\alpha) \simeq 250$ nm. After approaching the surface, the sample is scanned utilizing the $I_T$ feedback (tunneling mode), whereas local magnetic field are picked-up by the Hall probe (lift mode). An alternative way is to scan the surface at a fixed height, the sensor is lifted at a user defined distance from the sample and the image is acquired without the use of the STM feedback.

**SHPM test measurements**

Our SHPM microscope has been tested successfully down to $T = 2$ K and under magnetic field $H = 70$ kOe. In Fig. 2.15 is displayed a test image taken at $T = 100$ K on an hard disk sample showing the shape of the domain of magnetization. The color scale is utilized to evidence the intensity of the measured magnetic flux. The white color indicates the positive sign of the measured magnetic flux, hence domains with outgoing stray field $B_{sf}^z$. Conversely, the black color is used for domains with incoming stray field $B_{sf}^z$.

The SHPM technique is complementary to MFM in the study of the surface magnetization. Fig. 2.16 allows a comparison between these two techniques. A limitation of the SHPM microscopy is related to the resolution of the Hall probe which is smaller than the size of the object under investigation. In panel (a), the MFM image shows the labyrinthine pattern of the magnetic domain of a FePt thin film [114], which display pitch of $\simeq 140$ nm. The same sample is investigated by SPHM in panel (b): broaden spots are observed in this case, that results by the averaging effect of the Hall probe with resolution lower than the domain pitch.
2. Experimental methods and theoretical background

Figure 2.15: SHPM image of hard disk test sample \((T = 100 \text{ K})\). Area 14x14 \(\mu\text{m}^2\).

Figure 2.16: FePt domain pattern taken by (a) MFM and (b) SHPM.
The working principle of Focused Ion Beam (FIB) is similar to that of Scanning Electron Microscope (SEM), provided that ions instead of electrons are used as beam source. At the top of the FIB column, a series of electrodes, electron lenses and mechanical apertures extract charged particles from the Liquid Metal Ion Source (LMIS), a field-emission point-source that utilizes liquid Ga. The charged particles are focused into a beam with the desired characteristics: either a ”large” beam of high current or a ”small” beam of low current. The position of the beam over the sample is controlled by the deflection plates which provide the scanning feature. The key feature of LMIS is the high brightness, which allows to focus into a small beam a useful amount of current.

The basic process occurring when 30 keV Ga\(^+\) ions hit the sample is sputtering (Fig. 2.17(a)). Sample atoms, in different species (neutral, ions, metastable), are removed from the surface region as a result of a collisional cascade process generated by the incoming beam. The sputtering process with ion beams of nanometers size is the basis of FIB patterning at the nanoscale.

Due to the coincidence of FIB and SEM beams, the Dual Beam system (Fig. 2.17(b)) offers the unique capability of sculpting, patterning and fabricating structures at the nano- or micro-scale with the FIB and to analyze them simul-
taneously with the high resolution, non-destructive SEM probe (Fig. 2.18) [115]. The patterned surfaces of this thesis work were fabricated with a Dual Beam FIB-SEM facility (FEI-Strata DB 235M), having maximum beam power 30 keV, Ga\(^+\) source with 1 pA-20 nA current. The minimum spotsize is 7 nm. The SEM has a thermal emission source and 3 nm resolution in the 1-30 keV range.
Part II

Results
Chapter 3

Antiferromagnetic rings with substitution

In this Chapter I present the thermodynamic properties of a class of heterometallic molecular rings. This work allowed to understand the characteristics of these systems and it has been preparatory to more focused studies, which are described in Chapter 4 and 5 (also published in Ref. [116–118]).

My contribution to this work concerns measurements of specific heat and torque magnetometry. Chemical synthesis and characterization were performed in Manchester (G. Timco), and spin-Hamiltonian calculations were done in Parma (S. Carretta, P. Santini, G. Amoretti).

3.1 Heterometallic Cr$_7$M rings

3.1.1 Synthesis

The synthesis of molecular Cr$_7$M rings is described in Ref. [29]. Starting from the parent compound

$$\text{Cr}_8\text{F}_8(\text{O}_2\text{CCMe})_{16},$$

in short Cr$_8$, the anion

$$[\text{Cr}_7\text{MF}_8(\text{O}_2\text{CCMe}_3)_{16}]^-$$

was produced substituting Cr$^{3+}$ with a metallic dication M$^{2+} = \text{Cr}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Fe}^{2+}$ and Co$^{2+}$. To balance the negative charge, a proper
Figure 3.1: Structure of Cr$_7$Ni (others Cr$_7$M show similar characteristics). Colors: Cr, green; Ni, purple; Zn, orange; F, yellow; O, red; C, black; N, blue; H grey.
Heterometallic Cr₇M rings

Figure 3.2: ac-susceptibility $\chi T$-vs-$T$ of Cr₇M. (From Ref. [29])

cation

$$[R_2\text{NH}_2]^+$$

being $R=$Me, Et, nPr, nBu, $n$-octyl, was utilized, and finally the neutral salt was separated from the parent compound Cr₈ which remains in solution. The final result was

$$[R_2\text{NH}_2][\text{Cr}_7\text{MF}_8(\text{O}_2\text{CCMe}_3)_{16}],$$

Cr₇M in short.

X-ray diffraction studies show that the anion has ring-shaped structure similarly to Cr₈, whereas the $[R_2\text{NH}_2]^+$ group is H-bonded inside the ring cavity (Fig. 3.1). In the cyclic framework the metallic ion occupies the position at the vertex of a regular octahedron and are bonded by two carboxylate and one fluoride bridges. The ring is planar, metal-metal distance is 3.4 Å and the O-C-O angle range between $125^\circ$-$126^\circ$, while the Cr-F-Cr angle between $121^\circ$-$123^\circ$.

The Cr₇M clusters are packed in arrays of identical magnetic molecules, held together by means of Van der Waals forces. No inter-cluster paths are available. The final products of the synthesis are either crystals or dried powders. In the former the lattice symmetry is controlled by the counter-ion ($R$) chemistry. For instance, tetragonal crystals with millimeter-size were grown with $R=$Me.
3. Antiferromagnetic rings with substitution

3.1.2 Magnetic characterization

Different Cr$_7M$ derivatives, for which the spin of $M$ ions spans from $s = 0$ of Cd$^{2+}$ to $s = 5/2$ of Mn$^{2+}$ were synthesized (Table 3.1). ac-susceptibility, plotted as $\chi T$-vs-$T$ (Fig. 3.2), show that for $T = 300$ K the saturation values of Cr$_7M$ are sorted by $s(M^{2+})$ as expected in the uncoupled-ions regime. The behavior of $\chi T$ at low temperature displays a decrease of $\chi T$ indicative of the antiferromagnetic coupling between the metal centers (Fig. 3.2). Differently from Cr$_8$, where the AF interaction gives a perfect compensation of the Cr$^{3+}$ spin lattices and therefore singlet ground state at low temperature and zero field, here the presence of $M^{2+}$ results in uncompensated spin arrangement and, consequently, to ground state $S_0 \neq 0$.

<table>
<thead>
<tr>
<th>Cr$_7M$</th>
<th>$M^{2+}$</th>
<th>$s(M^{2+})$</th>
<th>$S_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_7$Cd</td>
<td>Cd$^{2+}$</td>
<td>0</td>
<td>3/2</td>
</tr>
<tr>
<td>Cr$_7$Zn</td>
<td>Zn$^{2+}$</td>
<td>0</td>
<td>3/2</td>
</tr>
<tr>
<td>Cr$_7$Mn</td>
<td>Mn$^{2+}$</td>
<td>5/2</td>
<td>1</td>
</tr>
<tr>
<td>Cr$_7$Cu</td>
<td>Cu$^{2+}$</td>
<td>1/2</td>
<td>1</td>
</tr>
<tr>
<td>Cr$_7$Fe</td>
<td>Fe$^{2+}$</td>
<td>2</td>
<td>1/2</td>
</tr>
<tr>
<td>Cr$_7$Ni</td>
<td>Ni$^{2+}$</td>
<td>1</td>
<td>1/2</td>
</tr>
<tr>
<td>Cr$_7$Co</td>
<td>Co$^{2+}$</td>
<td>3/2</td>
<td>0(?)</td>
</tr>
</tbody>
</table>

Table 3.1: List of the Cr$_7M$ clusters, with $M^{2+}$ divalent ion, $s(M^{2+})$ the spin of $M^{2+}$, and $S_0$ the total molecular spin.

The specific heat $C(T)$ of the Cr$_7M$ clusters is plotted in Fig. 3.3. Above $T \approx 4$ K all the curves are almost superimposed because the similar lattice contribution $C_{latt}$ is the leading term. All the clusters show a Schottky anomaly peaked at $T \approx 5$ K that can be attributed to the energy gap between the ground and the first excited multiplets ($\Delta_2 \approx 10$ K). A diversification of the $C(T)$ behavior is observed below 2 K: the specific heat of Cr$_7$Cd, Cr$_7$Mn and Cr$_7$Co displays a Schottky anomaly whereas the curves of Cr$_7$Ni and Cr$_7$Fe fall down toward zero. In the first case, the anomaly peaked at $T \approx 0.5$ K for Cr$_7$Cd and Cr$_7$Mn, and $T \approx 0.3$ K for Cr$_7$Cu and Cr$_7$Co, arise because of the zero-field splitting of the ground state (energy gap $\Delta_1 < 1$ K). In the second case, alternatively,
Figure 3.3: Zero-field specific heat of several Cr$_7$M derivatives. The lines represent the calculations of the Schottky anomalies for Cr$_7$Cd, which are evaluated with Eq. 2.23 for the zero-field splitting ($\Delta_1$) and the gap between ground and first excited multiplets ($\Delta_2$). The lattice contribution is estimated by means of Eq. 2.20.

Figure 3.4: Comparison between the specific heat (at $H=0$, 1 T) of: (a) Cr$_7$Ni and Cr$_7$Fe, (b) Cr$_7$Mn and Cr$_7$Cu. (c) $C(H,T)$ for Cr$_7$Co.
the anomaly is lacking because the ground state of these clusters is a Kramers doublet which cannot be split by the anisotropic terms of $\mathcal{H}$ (Eq. 1.5).

The first analysis of specific heat and susceptibility data indicates that the substitution of Cr$^{3+}$ with $M^{2+}$ successfully modifies the ground state accordingly to the extra-spin introduced by the $M^{2+}$ ion.\footnote{Further differences arise from the zero-field splitting of the ground state.} The Cr$_7M$ derivatives can be therefore classified in three sub-classes in relation to the ground state total spin: $S_0 = 3/2$ (Cr$_7$Cd, Cr$_7$Zn), $S_0 = 1$ (Cr$_7$Mn, Cr$_7$Cu) and $S_0 = 1/2$ (Cr$_7$Ni, Cr$_7$Fe).

This classification is also justified by specific heat measurements at $H = 1$ T (Fig. 3.4(a,b)). For the set with $S_0 = 1/2$ (Cr$_7$Ni and Cr$_7$Fe, Panel (a)) and $S_0 = 1$ (Cr$_7$Mn and Cr$_7$Cu, Panel (b)), $C(T,H)$ shows that clusters with the same $S_0$ have comparable properties, suggesting similarities in the low-energy levels pattern. For $S_0 = 3/2$ (Cr$_8$Cd and Cr$_8$Zn), I just mention that specific heat and Inelastic Neutron Scattering (INS) measurements provide results in very good agreement [119]. In the following I thus restrict the discussion to Cr$_7$Cd and Cr$_7$Mn, whereas Cr$_7$Ni data are analyzed in detail in Chapter 5.

Regarding the Cr$_7$Co, Fig. 3.4(c) shows $C(T,H)$ with magnetic field ranging from 0 to 7 T. At $H = 0$, the low temperature Schottky anomaly rules out the presence of pure singlet ground state that arise by $s$(Co$^{2+}$) = 3/2. At low temperature, the spin of Co$^{2+}$ is known to have $s = 1/2$ (Ref. [120]), and partial quenching of the orbital momentum is expected. Furthermore, the slight shift of the Schottky anomaly for $H \neq 0$, suggests the presence of low-lying multiplets due to small $J_{Cr-Co}$.

The specific heat $C(H,T)$ is displayed in Fig. 3.5 for Cr$_7$Cd and Fig. 3.6 for Cr$_7$Mn and Cr$_7$Cu. At first glance, the two set of data show the shift of the low temperature anomaly $\Delta_1$ toward high temperature as $H$ increases. Torque magnetometry is utilized to experimentally probe the magnetic anisotropy. Being Cr$_7M$ cyclic and planar, we can define $\hat{z}$ to be the direction perpendicular to the ring plane (and consequently the orthogonal directions $\hat{x}$ and $\hat{y}$), and $\theta$ to be the angle between $\hat{z}$ and the static magnetic field $\mathbf{H}$. I investigated a tetragonal single crystal that has been mounted on the torque platform having $\hat{z} \parallel \mathbf{H}$ at $\theta=0$. With reference to Fig. 2.7, I performed a $\tau_y$ vs $\theta$ measurement at $T = 2$ K and $H = 1$ T. The result is a sinusoid, as predicted for an uniaxial system (inset of Figs. 3.5 and 64)
Figure 3.5: (a) Specific heat $C/R$ of a thin pellet of pressed powders of Cr$_7$Cd as a function of the temperature ($T$) and magnetic field ($H$). Lines are results of theoretical calculations. Inset: torque signal measured on a 1x1x0.7 mm$^3$ single crystal of Cr$_7$Cd.

Figure 3.6: (a) Specific heat $C/R$ of a thin pellet of pressed powders of Cr$_7$Mn as a function of the temperature ($T$) and magnetic field ($H$). Lines are results of theoretical calculations. Inset: torque signal measured on a 1.6x1.3x0.5 mm$^3$ single crystal of Cr$_7$Mn. (b) Specific heat $C(H,T)$ of Cr$_7$Cu. It is worth noting the similar behavior of Cr$_7$Mn (a) and Cr$_7$Cu (b).
and 3.6(a)). The principal directions $\theta = 0^\circ, 90^\circ, 180^\circ$ and $270^\circ$ correspond to the alignment of the $\hat{z}$ and $\hat{x}$ axis along the $\mathbf{H}$ direction. For instance, the torque exerted for slightly off-perpendicular magnetic field orientation ($\theta \sim 90^\circ$) tends to align the ring axis to the direction of $\mathbf{H}$, this behavior therefore shows that the ground state of Cr$_7$Cd and Cr$_7$Mn has easy-axis anisotropy.

To obtain a quantitative analysis, we used a model spin Hamiltonian $\mathcal{H}$ of the form of Eq. 1.5. For Cr$_7$Cd, if we suppose that the divalent ion is placed in the site $i=8$, we can assume $J_8 = 0$ and $d_8 = 0$ because Cd$^{2+}$ is diamagnetic, while $J_i = J_{C\ell}$ and $d_i = d_{C\ell}$ for every $i \neq 8$. Next-nearest-neighbor (n. n. n.) interaction is expected to be weak in these systems and therefore is neglected. Indeed, in similar antiferromagnetic rings Fe$_7$Zn and Fe$_7$Mn it has been found by inelastic neutron scattering that n. n. n. interaction is 0.016 times smaller than nearest-neighbor coupling [121]. The magnetocrystalline anisotropy is considered neglecting the rhombic term in Eq. 1.3. The eigenstates of $\mathcal{H}$ allows to calculate the specific heat utilizing Eq. 2.23, while the lattice contribution is evaluated by means of Eq. 2.20. The best fit of the specific heat is obtained for $J/k_B = 15.3$ K and $d/k_B = -0.31$ K (Fig. 3.5). The sign of $d_{C\ell}$ is obtained directly by the torque measurement which is consistent to $d_{C\ell} < 0$. These parameters are in good agreement with those obtained by INS spectra (taken on Cr$_7$Zn) $J_{C\ell}/k_B = 16.6$ K and $d_{C\ell}/k_B = -0.32$ K [119], and EPR measurements [29]. They are also similar with those obtained in the Cr$_8$ cluster ($J_{C\ell}/k_B = 16.9$ K, $d_{C\ell}/k_B = -0.34$ K) [19], thus confirming that the substitution of one Cr ion does not drastically change the ligand fields and the exchange interactions of the other unsubstituted ions. The EPR experiment reveals the presence of a small rhombic term which has been neglected in the diagonalization procedure since it does not significantly affect the pattern of the low lying states. The lattice parameters determined by specific heat are $\Theta_D = (157 \pm 10)$ K and $\delta = 0.42$ K$^{-1}$ (with $r = 289$).

Regarding the Cr$_7$Mn, the calculations give $J_{C\ell-C\ell}/k_B = 16.9$ K, $J_{C\ell-Mn}/k_B = 15.9$ K, $d_{C\ell}/k_B = -0.35$ K, $d_{Mn}/k_B = 0.01$ K (a factor two-hundred smaller that the Ni case, see Section 5.1.1), $\Theta_D = (152 \pm 10)$ K and $\delta = 0.36$ K$^{-1}$ (with $r = 289$). In order to correctly reproduce the shape of the low-temperature Schottky anomaly of $C(H=0,T)$ (Fig. 3.6), the rhombic term of Eq. 1.3 must be considered. If the $S$-mixing is neglected, the zero-field splitting describing the
Heterometallic Cr$_7$M rings

Figure 3.7: Energy levels pattern calculated for Cr$_7$Cd (a) and Cr$_7$Mn (b) after the diagonalization of the Hamiltonian operator. The calculation is performed considering an angle $\theta$ between $\mathbf{H}$ and $\hat{z}$. 
anisotropic term splitting of the $S = 1$ ground multiplet can be obtained by projecting the complete Hamiltonian onto the corresponding subspace. We thus obtain $\mathcal{H}_{S=1} = D(S_z^2 - S(S + 1)/3 + E(S_x^2 - S_y^2))$ with rhombicity $E/D = 0.14$. Inelastic neutron scattering experiments are consistent with our results [119]. I just mention that the preliminary analysis of the specific heat of Cr$_7$Cu indicates that the rhombic term is negligible in that case.

The pattern of the energetic levels of Cr$_7$Cd and Cr$_7$Mn is depicted in Fig. 3.7. The Cr$_7$Cd displays ground state quadruplet split by axial anisotropy in two doublets $|S = 3/2, M = \pm 1/2\rangle$ and $|S = 3/2, M = \pm 3/2\rangle$. The energy of $|S = 3/2, M = \pm 3/2\rangle$ is lowered because of the easy-axis anisotropy. The first excited level ($S = 1/2$) is observed at $\Delta_2 \simeq 10$ K, whereas higher $S = 5/2$ multiplet is found at 20 K.

The Cr$_7$Mn displays $S = 1$ ground state. Anisotropy terms split the triplet in three levels having $|S = 1, M = -1\rangle$, $|S = 1, M = 0\rangle$ and $|S = 1, M = +1\rangle$. The former is favored because of easy-axis. The first excited multiplet has barycenter at $\Delta_2 \simeq 20$ K.

### 3.1.3 Conclusions

In conclusion, I presented the study of a class of heterometallic antiferromagnetic rings whose magnetic properties can be controlled by substituting a chromium site with a divalent transition metal. Magnetic characterization has been performed by means of specific heat and torque magnetometry. The derivatives are classified in three sub-classes accordingly to the ground state having $S_0 = 1/2$, 1 and 3/2. The experimental properties are well reproduced by the Hamiltonian Eq. 1.5 and the parameters obtained are in good agreement with the results of inelastic neutron scattering (Ref. [119]).
Chapter 4

Elementary excitations in antiferromagnetic Heisenberg spin segments.

Molecular (Cr₆)₂, (Cr₇)₂, Cr₃Cd and (NiCr₆)₂Zn are derivatives having the same template structure of Cr₈ and Cr₇M (two-carboxilates and one fluoride bridges between metal sites). These systems can be regarded as spin segments, so they constitute the model system to investigate the nature of the spin excitations in antiferromagnetic chains with finite size.

In this Chapter I discuss the result I obtained by susceptibility, magnetization and specific heat experiments. For sake of simplicity and to permit a direct comparison between the different system, the data are analyzed introducing solely an exchange constant $J$ for each cluster. This approximation describes well the behavior of the discussed system.

My contribution to this work concerns the magnetic measurements. Chemical synthesis and characterization were performed in Manchester (G. Timco), and spin-Hamiltonian calculations were done in Parma (S. Carretta, P. Santini, G. Amoretti).
4. Elementary excitations in antiferromagnetic Heisenberg spin segments.

4.1 Cr-based AF spin segments

4.1.1 Experimental details

Starting from the synthetic approach that yields Cr₈, a new class of heterometallic derivatives are obtained [29,30,123,124] and they can be regarded as ”broken” or ”open” spin rings. These systems are obtained by bridging trivalent metal (mainly Cr³⁺) ions with carboxylate and fluoride ligands that results in antiferromagnetic exchange coupling between two neighboring spin centers. In a first synthetic route, non magnetic Cd²⁺ or Zn²⁺ were substituted to a Cr³⁺ in Cr₈ thus breaking the symmetry of the ring. Broken Cr₈M, with M=Ni, Cd, rings are also obtained and they comprise an even number of spin centers [123,125]. In a further synthetic route, finite Cr³⁺ segments have been synthesized with characteristic shape of two ”horseshoe” facing one another [30]. Each ”horseshoe” may result either even-membered or odd-membered. Furthermore, heterometallic chains have also been synthesized were a Ni²⁺ is positioned at the end of a Cr₆ segment. This compound (NiCr₆)₂Zn, is composed by two NiCr₆ moities attached through a non-magnetic Zn²⁺ in a S-shaped ”seahorse” cluster.

The crystal structures of the molecules studied in this work are shown in Fig. 4.1.

\[
[(H₂NR₂)₃Cr₆F₁₁(O₂CCMe₃)₁₀(H₂O)]₂,
\]

with \( R = C₃H₇ \), in short (Cr₆)₂, was prepared as reported in Ref. [30].

\[
[(H₂NR₂)₃Cr₇F₁₂(O₂CCMe₃)₁₂(H₂O)]₂,
\]

with \( R = iC₃H₇ \), in short (Cr₇)₂, was prepared similarly to (Cr₆)₂ [126].

\[
[H₂NtBuisPr][Cr₈CdF₉(O₂CCMe₃)₁₈],
\]

in short Cr₈Cd, was obtained by the method given in Ref. [123].

\[
[Ni(cyclen)₂Cr₁₂ZnF₁₈(O₂CCMe₃)₂₄],
\]

in short (NiCr₆)₂Zn, is synthesized following Ref. [122]. The result is isostructural with

\[
[Ni(cyclen)₂Cr₁₂NiF₁₈(O₂CCMe₃)₂₄],
\]
Figure 4.1: Structure of: (a) (Cr$_6$)$_2$. (b) (Cr$_7$)$_2$. (c) Cr$_8$Cd. (d) (NiCr$_6$)$_2$Zn. Colours: Cr, green; Ni, purple; Cd, pale blue; Zn, orange; F, yellow; O, red; C, black; N, blue. H-atoms omitted for clarity.
in short (NiCr₆)₂Ni, reported in [127].

As a common feature, each Cr⁺³ ion has quenched orbital momentum and carries spin $s=3/2$ [128] while each Cr-Cr pair is linked by one fluorine ion and two carboxylates bonds. The O-C-O angle range between 120°-130° while Cr-F-Cr between 121°-125° from one derivative to another. This relatively small variation suggests that the magnetic coupling between two nearest neighboring Cr ions should be similar/comparable in all these compounds. In (Cr₆)₂ and (Cr₇)₂ (Fig. 4.1(a) and (b) respectively), we can recognize two “horseshoes” facing one another with H-bonds in between: the latter are known to be ineffective in producing magnetic coupling, hence the two horseshoes are expected to be magnetically uncoupled as confirmed by magnetic data analysis (see below). (NiCr₆)₂Zn (Fig. 4.1(d)) can be regarded as two independent NiCr₆ moieties, if one neglects the coupling between the non magnetic Zn²⁺ and the nearest neighbor Cr ions. Each NiCr₆ moiety presents six Cr⁺³ antiferromagnetically coupled with an external Ni²⁺ ion ($s=1$) bridged by one carboxylate and one fluorine. The remaining Cr₈Cd (Fig. 4.1(c)), can be regarded as a Cr-based ring broken
Cr-based AF spin segments

Figure 4.3: Magnetic field dependence of magnetization $M$ vs $H$ measured with a dc extraction magnetometer on powders. $M$-vs-$H$ curves show a different behavior between the even and odd spin segments at 2 K: The former (Cr$_6$ and Cr$_8$Cd) have $S = 0$ ground state and low-lying excited levels close in energy and therefore populated at $T = 2$ K, the second one (Cr$_7$) have a well defined $S = 3/2$ ground state at 2 K. Lines are results of theoretical calculations. The powder magnetization has been numerically calculated by averaging over all possible orientations of the field.

by a nonmagnetic Cd ion [123].

4.1.2 Results

On the basis of the structural features of (Cr$_6$)$_2$, (Cr$_7$)$_2$ and (NiCr$_6$)$_2$Zn previously discussed, it is convenient to normalize and compare values referred to single moieties, hence, in the following, data per formula unit have been further divided by two, so I simply refer to Cr$_6$, Cr$_7$ and NiCr$_6$. Fig. 4.2 shows results of ac-susceptibility measurements plotted as $\chi T$ vs $T$. The room temperature $\chi T$ values approach that expected for non-correlated spins (Eq. 2.6) with $g_{Cr} \simeq 2$, i.e., $\chi T \simeq 11.2$ emu K mol$^{-1}$, 13.1 emu K mol$^{-1}$, 15.0 emu K mol$^{-1}$ and 12.2 emu K mol$^{-1}$ for Cr$_6$, Cr$_7$, Cr$_8$Cd and NiCr$_6$ respectively.

At low temperature, the susceptibility curves evidence the different behavior of the even and odd spin segments: while for the even ones, i.e. Cr$_6$ and Cr$_8$Cd,
4. Elementary excitations in antiferromagnetic Heisenberg spin segments.

\[\chi_T\] falls to zero indicating a singlet \(S = 0\) ground state, in the case of odd spin segments, i.e. \(\text{Cr}_7\) and \(\text{NiCr}_6\), a \(S \neq 0\) ground state is observed. The fact that \(\chi_T\) in \(\text{Cr}_7\) tends to saturate for \(T < 4\) K, suggests that the ground state is energetically well separated from the higher ones and the susceptibility value \(\chi_T(2\,\text{K}) = 2.1\,\text{emu K mol}^{-1}\) points to \(S = 3/2\) ground state of each moiety. The low temperature susceptibility value \(\chi_T(2\,\text{K}) = 1.2\,\text{emu K mol}^{-1}\) of \(\text{NiCr}_6\) is consistent with a \(S = 1\) ground state as expected for one uncompensated \(s = 1\) of \(\text{Ni}^{2+}\).

Consistently with the ac susceptibility behavior, the magnetization \(M\)-vs-\(H\) curves of Fig. 4.3 show different behavior for even and odd spin segments. For \(\text{Cr}_7\) a Brillouin-like curve is observed at \(T = 2\) K, indicating that the excited states are energetically apart and not populated. The saturation value \(M \approx 3\,\mu_B\) points to a \(S = 3/2\) ground state, in agreement with low temperature ac susceptibility. Conversely, for the even membered spin segments, the magnetization at \(T = 2\) K is continuously increasing suggesting the presence of low-lying \(S \neq 0\) excited states close in energy to the ground state, that are significantly populated at this

Figure 4.4: The temperature dependence of the specific heat \(C(H, T)\) normalized to the gas constant \(R\), for (a) \(\text{Cr}_6\) and (b) \(\text{Cr}_8\text{Cd}\). The low temperature Schottky anomaly is related to the energy gap between the ground states and the excited multiplets. Above \(T \sim 4\) K the lattice specific heat is the leading contribution. Lines are results of theoretical calculations.
Figure 4.5: The temperature dependence of the specific heat $C(H, T)$ normalized to the gas constant $R$, for Cr$_7$. The low temperature Schottky anomaly is related to the zero field splitting of the $S = 3/2$ ground state. Above $T \sim 4$ K the lattice specific heat is the leading contribution, while the $H$ dependence of the curves is due to the Schottky anomaly between first excited and ground state. Lines are results of theoretical calculations.

temperature and that progressively contribute by increasing the magnetic field strength.

The low-temperature specific heat of molecular spin clusters typically exhibits characteristic Schottky anomalies related to the energy gaps between the lowest lying energy levels, while at high temperature this magnetic contribution is overwhelmed by the lattice one [103]. Just to get familiar with these curves, one may notice that for Cr$_6$ (Fig. 4.4)(a) and Cr$_8$Cd (Fig. 4.4)(b) the low-temperature Schottky anomaly in zero field is mainly characterized by the energy gap between the lowest singlet and the first excited ($S = 1$) state. Reminding that the maximum of the anomalies (1.3 K and 1.1 K for Cr$_6$ and Cr$_8$Cd respectively) occurs at $\sim 0.4$ of the energy gap between the singlet and the barycenter of the triplet, it is easy to see that excited states are significantly populated at $T = 2$ K and this intuitively explains the observed behavior of the magnetization (Fig. 4.3). Regarding the odd segments, the low temperature Schottky anomaly measured at $H = 0$ in Cr$_7$ (Fig. 4.5) is due to the zero field splitting of the ground state.
Even before any deeper data analysis, it is worth noting the similarity between the specific heat of Cr$_7$ (Fig. 4.5) and that of Cr$_7$Cd [116]. This confirms that, in spite of the different structures, these two compounds well represent segments of 7 spins $s$=3/2 with quite similar energy spectrum.

To obtain a quantitative analysis, we use a model spin Hamiltonian of the form of:

$$\mathcal{H} = \sum_{i=1}^{n-1} J_i \mathbf{s}_i \cdot \mathbf{s}_{i+1} + \sum_{i=1}^{n} d_i (s^2_i(i) - s_i(s_i + 1)/3) + \mu_B \sum_{i=1}^{n} g_i \mathbf{H} \cdot \mathbf{s}_i,$$

(4.1)

where $n$ is the number of spin centers. The first term is the dominant isotropic Heisenberg exchange, where $J_i$ is the exchange Heisenberg coupling, the second term describes the local crystal field, and the last one is the Zeeman term related to the applied magnetic field $\mathbf{H}$. Next-nearest-neighbor (n.n.n.) interaction is expected to be weak in these systems and therefore are neglected. Indeed, in similar antiferromagnetic rings Fe$_7$Zn and Fe$_7$Mn it has been found by inelastic neutron scattering that n.n.n. interactions are 0.016 times smaller than nearest-neighbor coupling [121]. Respect to Eq. 1.5, in Eq. 4.1 we have neglected dipolar intra-cluster interaction (Eq. 1.4) for two reasons: on the one hand, the addition of such a term requires to know the actual spatial orientation of the $\hat{z}$-axis with respect to the unit cell axes. Being measurements performed on powders, this piece of information is unavailable. On the other hand, on these measurements virtually all effects of dipolar interactions are undistinguishable from those of the local crystal fields and therefore dipolar interactions can be omitted provided the $d_i$ parameters are understood as renormalized ones.

The diagonalization of Eq. 4.1 allows to theoretically reproduce the properties of the different compounds by means of Eq. 2.7 and Eq. 2.23. In the calculation of $M(H)$, anisotropic terms have been included and the powder magnetization has been numerically obtained by averaging over all the possible orientation of the field. The choice of the number of free parameters has some degree of arbitrariness and it depends on the level of required precision. For each compound, we consider only one coupling constant $J_{Cr-Cr}$ between neighboring Cr spin centres since the introduction of further constants, although it may occasionally improve the quality of data fit, does not change the discussion on the spin excitations that will be presented in the next paragraph. Since measurements were performed
Figure 4.6: Lowest energy levels of the exchange part of the Hamiltonian Eq. 4.1 for Cr₆, Cr₇, Cr₈, and Cr₈Cd. Note that the lowest $L$-band has a quasi parabolic $S$-dependence.

Figure 4.7: Lowest energy levels of the exchange part of the Hamiltonian Eq. 4.1 for NiCr₆.
on powder samples, precision on the determination of anisotropy parameters is also limited to 30%. Within this level of accuracy, it is worth to stress that the simultaneous fit of the $\chi$, $M$-vs-$H$ and $C(T, H)$ curves was proved to be a very powerful tool and, in the case of Cr$_6$, Cr$_7$ and Cr$_8$Cd, allows to identify and fix one set of microscopic parameters for each derivative, as reported in Table 4.1. It turns out from the comparison of results that the exchange and anisotropy constants are very similar in the molecular spin segments here studied, confirming what expected from the similar chemical environment and links between metal ions. Recently, inelastic neutron scattering experiments have been performed on some of these derivatives and similar $J$ values have been obtained [129], consistently with our experimental data analysis. In summary, these results validate the view of these compounds as different variants of spin segments and they allow direct comparison of energy spectra, as presented in the next paragraph.

<table>
<thead>
<tr>
<th></th>
<th>$J_{Cr-Cr}$ (K)</th>
<th>$d_i$ (K)</th>
<th>$g_i$</th>
<th>$\Theta_D$ (K)</th>
<th>$\delta$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$_6$</td>
<td>13.8</td>
<td>-0.3</td>
<td>$g_{Cr}=1.98$</td>
<td>146</td>
<td>0.25</td>
</tr>
<tr>
<td>Cr$_7$</td>
<td>13.6</td>
<td>-0.3</td>
<td>$g_{Cr}=1.98$</td>
<td>174</td>
<td>0.32</td>
</tr>
<tr>
<td>Cr$_7$Cd</td>
<td>16.9</td>
<td>-0.3</td>
<td>$g_{Cr}=1.98$</td>
<td>157</td>
<td>0.42</td>
</tr>
<tr>
<td>Cr$_8$</td>
<td>16.9</td>
<td>-0.3</td>
<td>$g_{Cr}=1.98$</td>
<td>154</td>
<td>0.37</td>
</tr>
<tr>
<td>Cr$_8$Cd</td>
<td>14.8</td>
<td>-0.3</td>
<td>$g_{Cr}=1.98$</td>
<td>168</td>
<td>0.25</td>
</tr>
<tr>
<td>NiCr$_6$</td>
<td>13.8</td>
<td>-</td>
<td>$g_{Cr}=2.03$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NiCr$_6$</td>
<td>13.8</td>
<td>-</td>
<td>$g_{Ni}=2.03$</td>
<td>-</td>
<td>-</td>
</tr>
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</table>

Table 4.1: List of the parameters obtained by the fit of the experimental data. Cr$_8$ data are taken from [19]. For NiCr$_6$ $g_{Ni} = g_{Cr}$ has been assumed.

### 4.1.3 Discussion

In the following, I discuss some general features of the low-lying energy spectrum of spin segments. We first focused on the eigenstates of the dominating exchange part of the Hamiltonian, which are shown in Fig. 4.6 for the ”broken” Cr$_8$Cd ring, even and odd spin segments Cr$_6$, and Cr$_7$ and, for comparison, for the ”closed” Cr$_8$ ring. Later I will clarify the role and some effects of the anisotropy term.
Figure 4.8: Component $W_N \equiv |\langle G|N \rangle|^2$ of the ground state $|G\rangle$ onto one of the two Néel states $|N\rangle$ as a function of the $d/J$ ratio. For Cr$_7$ the ground state is doubly degenerate and the curve refers to one of the two components. Horizontal dashed curves represent the limit to which the curves tend for large $d/J$, i.e., 1 for Cr$_7$ and 0.5 for all remaining segments. It is apparent that for the observed ratio $-d/J \simeq 0.02$ the ground state composition is almost the same as for $d/J = 0$.

At first glance, the concept of rotational ($L$) band, which was introduced for AF closed rings, appears to be applicable to the open segments as well. This is suggested by the roughly parabolic form of the energy vs $S$, i.e. the $E(S)$ curve for the lowest-$S$ multiplets, and it is more quantitatively demonstrated by the composition of the corresponding eigenstates. $L$-band states in closed rings are characterized by the property that the moduli of the total spin of the two sublattices, $S_A(S_A + 1)$ and $S_B(S_B + 1)$, are to a great extend locked in their maximum value, i.e. the eigenstates have the structure $|S_A = n_A s, S_B = n_B s, S_{tot} = |S_A - S_B|\ldots (S_A + S_B)\rangle$. For instance, for the the lowest-lying $S = 1$ state in Cr$_8$Cd the weight of $|S_A = 6, S_B = 6, S_{tot} = 1\rangle$ is about 69%. In even-numbered rings the remaining weight in $L$-band eigenfunctions is large on states of type $|S_A = S_B, S_{tot} = 0\ldots 2S_A\rangle$, i.e., the sublattice spin-lengths are mainly locked into their maximum value, and sublattice-spin fluctuations occur jointly.

Table 4.2 shows that the lowest eigenstates in the present systems actually have a dominating $L$-band-type component and that this holds for the heterometallic NiCr$_6$ segment as well (see also the spectrum in Fig. 4.6, 4.7). The weight of this component has to reach, of course, the limiting value of one for the ferromagnetic
multiplet but it does not always do so in a monotonic way. In addition, for a given number of spins the ring opening makes the Landé picture less precise since AF correlations between sublattices are less enforced. Indeed, the \( L \)-type component in the ground low-lying states of \( \text{Cr}_8\text{Cd} \) is smaller than in \( \text{Cr}_8 \). According to the Landé rule \( \Delta = (2J/n)S(S + 1) \), the energy separation between levels, is expected to scale as \( (2J/n) \), thus inversely proportional to the number \( n \) of spin sites. we just notice from Fig. 4.6 that the spectrum of lowest lying states of \( \text{Cr}_6 \) actually reproduces that of \( \text{Cr}_8\text{Cd} \), apart from a multiplicative factor \( 8/6 \sim 1.3 \), in agreement with the ratio between \( 1/n=1/6 \) and \( 1/8 \) for the two spin systems respectively.

Since the the zero field Schottky anomaly in the specific heat are directly related to the energy gap between the ground state and the first excited states, it provides a simple but direct test of applicability of the model on this family of molecular compounds and, in turns, of the flexibility of the molecular route to provide model systems. In odd-membered spin segments we may notice that the lowest state has not the lowest spin value, namely in \( \text{Cr}_7 \) and \( \text{NiCr}_6 \) the lowest states are \( S = 3/2 \) and \( S = 1 \) respectively (see Fig. 4.6). Model calculations show that the energy gap between the ground state and first excited states of \( \text{Cr}_7 \) (having \( S = 1/2 \)) is actually of few K while in even membered spin segments this is smaller. This explains why magnetization and specific heat below 4 K are well characterized by the ground state solely in odd-membered cases while excited states are well populated and contribute to determine the properties of the even membered spin segments at these temperatures, in spite of the fact that the \( J \) constants are similar in all these molecular compounds.

<table>
<thead>
<tr>
<th></th>
<th>( \text{Cr}_8 )</th>
<th>( \text{Cr}_8\text{Cd} )</th>
<th>( \text{Cr}_6 )</th>
<th>( \text{Cr}_7 )</th>
<th>( \text{NiCr}_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S = S_0 )</td>
<td>0.83</td>
<td>0.79</td>
<td>0.9</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>( S = S_0 + 1 )</td>
<td>0.83</td>
<td>0.69</td>
<td>0.8</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>( S = S_0 + 2 )</td>
<td>0.84</td>
<td>0.59</td>
<td>0.71</td>
<td>0.81</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Table 4.2: Component of the lowest-lying eigenstates for three values of the total spin \( S \) onto the Landé-type state \( |S_A = n_A S, S_B = n_B S, S_{\text{tot}} = S\rangle (|S_A = 11/2, S_B = 9/2, S_{\text{tot}} = S\rangle \) for the heterometallic \( \text{NiCr}_6 \). \( S_0 \) is the ground-state total spin (\( S_0 = 0 \) in \( \text{Cr}_8 \), \( \text{Cr}_8\text{Cd} \) and \( \text{Cr}_6 \), \( S_0 = 3/2 \) in \( \text{Cr}_7 \), \( S_0 = 1 \) in \( \text{NiCr}_6 \)).
As far as the $E$-band is concerned, in closed rings these states are characterized by a dominating contribution in which the total spin of the two sublattices differ by one. In terms of the translational (cyclic) symmetry of rings these states belong to representations with wavevector $k \neq 0, \pi$ and are therefore degenerate in $k, -k$ pairs. The main effect of the ring opening is the splitting of this degeneracy, which can be sizeable in short segments: this is evident, for instance, by directly comparing the spectrum of the "broken" Cr$_8$Cd ring with that of closed Cr$_8$ ring (Fig. 4.6).

In the previous section we determined the single ion anisotropy parameters $d$ for Cr$_6$, Cr$_7$, Cr$_8$Cd and it turns out that these are much smaller than the Heisenberg coupling constants $J$. Since this is one relevant feature of the model that well describes our experiments, it naturally leads us to the conclusion that these -or similar- molecules can actually be used as model system for studying finite Heisenberg chains. In order to see to what extent this picture holds and clarify the role of anisotropy term, we note that for a generic value of the applied field the effect of the anisotropic terms (as determined in the previous section) on the eigenstates is not qualitatively important and mostly consists in a first-order splitting of the various $S$-multiplets into symmetry-adapted states.

If one focus on the ground state, a compact and physically motivated way...
to quantify how much anisotropy modifies its composition is to calculate the weight \((W_N)\) in this state of the two Néel components, where all spins are aligned along the \(\hat{z}\)-axis but in opposite directions on the two sublattices. Indeed, being anisotropy of easy-axis type, in segments with integer total spin for a large enough \(d/J\) ratio \(W_N \to 0.5\) and the ground state becomes a superposition of the two Néel states. In this limit, a tunnelling picture for the Néel vector holds. In segments with half-integer total spin, such as \(\text{Cr}_7\), the ground state is always at least doubly degenerate by Kramers theorem if \(H = 0\). For large enough \(d/J\) ratio each state of the ground doublet approaches either of the two Néel states, \(W_N \to 1\) and no tunnelling occurs. Fig. 4.8 shows \(W_N\) calculated for \(\text{Cr}_6\), \(\text{Cr}_7\), \(\text{Cr}_8\) and \(\text{Cr}_8\text{Cd}\). It is apparent that for the \(d\) values determined by experiments, the ground state is very close to that of the isotropic Heisenberg model in all molecules. The Néel limit is only reached for \(d \gg J\).

In order for anisotropy to play a qualitatively important role on the states composition it is necessary that inter-multiplet splittings be comparable or smaller than the anisotropy strength. In particular, for the ground-state this occurs whenever the applied field \(H\) produces a crossing between levels belonging to different multiplets of the exchange part of the Hamiltonian (Eq. 4.1). It has been shown that in \(\text{Cr}_7M\) \((M=\text{Ni, Cd})\) the anisotropy turns such crossing into anticrossings (ACs), which physically correspond to quantum oscillations of the molecule’s total-spin [117,119,131]. On the other hand, crossings are observed in the \(\text{Cr}_8\) ring. Among the present spin segments, \(\text{Cr}_8\text{Cd}\) and \(\text{Cr}_6\) behave like the \(\text{Cr}_8\) ring, whereas \(\text{Cr}_7\) and \(\text{NiCr}_6\) are characterized by ACs (see Fig. 4.9). This difference in behavior reflects different symmetry properties of the Landé states in the two cases: in \(\text{Cr}_8\text{Cd}\) and \(\text{Cr}_6\), like in \(\text{Cr}_8\), the \(L\)-band states which cross belong to different irreducible representations of the permutation symmetry of the chain and therefore they are not allowed to mix. On the contrary, they do belong to the same representation in \(\text{Cr}_7\) and \(\text{NiCr}_6\) where they mix and produce ACs. This difference might be experimentally demonstrated by single-crystal low-\(T\) torque measurements. The calculated \(H\)-dependence of the torque is characterized by the usual step-like behavior at the crossings for \(\text{Cr}_6\) and \(\text{Cr}_8\text{Cd}\), whereas it peaks for \(\text{Cr}_7\) and \(\text{NiCr}_6\).
4.1.4 Conclusions

In conclusion, we have investigated ac-susceptibility, low temperature magnetization and specific heat of different molecules whose magnetic core represent variants of spin segments. Spin-Hamiltonian (Eq. 4.1) with dominant Heisenberg antiferromagnetic term, fits well the experimental data, indicating that these molecular compounds are actually very close to a collection of identical and non-interacting Heisenberg segments, whereas anisotropy plays a minor role. We believe that the synthesis of similar and longer molecular AF chains will offer a unique opportunity to investigate topological size effects characteristic of the one-dimensional Heisenberg model.
4. Elementary excitations in antiferromagnetic Heisenberg spin segments.

Figure 4.10: Structure of (Cr₆Cu)₂. Colours: Cr, green; Cu, orange; F, yellow; O, red; C, black; N, blue; H, grey.

4.2 Cu twins linked by Cr-based segments

The approach used to synthesize the Cr₈ derivatives has been replied to realize clusters with the same template structure but higher nuclearity and different shape. A novel class of cyclic systems (CrₓCu)₂ (x = 5, 6, 7) was recently synthesized [130], nominally:

\[(C₇H₆N₂H₂)₂[Cr₈Cu₂F₁₄(O₂CCMe₃)₁₆(C₇H₆N₂)₂](HO₂CCMe₃)₂,\]
in short (Cr₄Cu)₂;

\[[(C₈H₁₅)₂NH₂]₂[Cr₁₀Cu₂F₁₄(O₂CCMe₃)₂₂],\]
in short (Cr₅Cu)₂; and

\[[\text{isoC}_₃H₇]₂(C₂H₅)NH]₂[Cr₁₂Cu₂F₁₆(O₂CCMe₃)₂₆],\]
in short (Cr₆Cu)₂. In these molecules two Cu²⁺ (s = 1/2) are linked by Cr³⁺ (s = 3/2) segments to form an ellipsoidal cluster. In Fig. 4.10 is depicted the structure of (Cr₆Cu)₂, as obtained by X-ray diffraction (8 and 10-nuclear (Cr₄Cu)₂
Cu twins linked by Cr-based segments

Figure 4.11: (a) ac-susceptibility plotted as $\chi T$ vs $T$. Measurements were taken with $h_{ac} = 10$ Oe and frequencies 90, 1730, 9300 Hz on powders. No dependency on frequency was observed. (b) Magnetic field dependence of magnetization $M$-vs-$H$ measured at $T = 2$ K with a dc-extraction magnetometer on powders.

Figure 4.12: The temperature dependence of the specific heat $C(H,T)$ normalized to the gas constant $R$, for (a): (Cr$_4$Cu)$_2$ and (Cr$_6$Cu)$_2$, and (b): (Cr$_5$Cu)$_2$. 
4. Elementary excitations in antiferromagnetic Heisenberg spin segments.

and (Cr$_5$Cu)$_2$ show similar characteristics). Likewise to the parent Cr$_8$ parent compound, the Cr-Cr bond is realized by means of two carboxilates and one fluoride bridges, whereas Cu-Cr bond is realized by two carboxilates bridges on the one side, and one carboxilate and one fluoride on the other side. The Cr-Cu exchange coupling is thus expected to be weaker than Cr-Cr.

ac-susceptibility $\chi T$-vs-$T$ is plotted in Fig. 4.11(a). The room temperature $\chi T$ saturation value $\chi T \simeq 13.6$ emu K mol$^{-1}$, 17.6 emu K mol$^{-1}$ and 20.7 emu K mol$^{-1}$, respectively for (Cr$_4$Cu)$_2$, (Cr$_5$Cu)$_2$ and (Cr$_6$Cu)$_2$, is in agreement to that expected for uncorrelated paramagnetic ions. For (Cr$_4$Cu)$_2$ and (Cr$_6$Cu)$_2$, the low-temperature behavior of $\chi T$ points to ground state $S = 1$, while for (Cr$_5$Cu)$_2$ the product $\chi T$ progressively decreases. These results suggest AF coupling within the cyclic structure. In the first case the chromium segments are even-membered and the spins of the Cu$^{2+}$ lies parallel. The total spin of the complex results therefore $S = 1$. In the second case, conversely, the chromium segments is odd-membered and the AF coupling gives rise to a pattern of low lying states close in energy.

In Fig. 4.11(b) it is shown the dc-magnetization $M$-vs-$H$ taken at $T = 2$ K. For (Cr$_4$Cu)$_2$, the behavior at $H = 7$ T shows that $M$ is close to the saturation value $M_S \simeq 2 \mu_B$, which is expected for a well-defined $S = 1$ ground state. For (Cr$_5$Cu)$_2$ and (Cr$_6$Cu)$_2$, the shape of $M$-vs-$H$ suggests the presence of low-lying excited states that are already populated at this temperature and field.

Low temperature specific heat is shown Fig. 4.12. The $C(T)$ curves of (Cr$_4$Cu)$_2$ and (Cr$_6$Cu)$_2$ for $H \leq 3$ T are reported in panel (a): the analogy of the two set of curves indicates that (Cr$_4$Cu)$_2$ and (Cr$_6$Cu)$_2$ display a similar pattern of the lowest energy levels. Significant discrepancies arise at higher field when the excited states are involved, as it is also indicated by the magnetization at $T = 2$ K (Fig. 4.11(b)). Smaller gap between ground and first excited multiplets is indeed expected for (Cr$_6$Cu)$_2$ $(n = 14)$ respect to (Cr$_4$Cu)$_2$ $(n = 10)$ because of the factor $1/n$ of Landé rule Eq. 1.2. The Schottky anomaly observed at low temperature and $H = 0$ is related to the splitting of the ground triplet due to the magnetocrystalline anisotropy, whose strength differs in the two derivatives.

Concerning the specific heat of the cluster of (Cr$_5$Cu)$_2$ (Fig. 4.12), the overall behavior of $C(H, T)$ indicates also the presence of low-lying excited states.
In conclusion, in this section I discussed the characterization of a novel class of heterometalic systems (Cr\textsubscript{x}Cu\textsubscript{2})\textsubscript{2} (\(x = 4, 5, 6\)) where two Cu\textsuperscript{2+} (\(s = 1/2\)) ions are linked by chromium segments. Because of the specular features of the clusters, the low temperature properties are defined by the parity of \(x\): when \(x\) is even the copper twins are aligned ferro and the total spin of the ground state is \(S = 1\); when \(x\) is odd the copper twins are aligned antiferro hence \(S = 0\).
4. Elementary excitations in antiferromagnetic Heisenberg spin segments.
Chapter 5

Antiferromagnetic molecular rings for quantum computation

In Chapter 3 I discussed the magnetic properties of the series of Cr$_7M$ clusters, here I focalize on Cr$_7$Ni to discuss its characteristics in the framework of quantum computation (Section 5.1). In Section 5.2 I introduce the Cr$_9$Ni, that is a decanuclear system which displays properties similar to Cr$_7$Ni. Section 5.3 reports the results of the investigation of molecular dimers that we realized to create entangled states between spin-cluster qubits.

In this context, my work concerned the magnetic measurements, while synthesis and calculations were performed, respectively, at the University of Manchester and University of Parma. Dr. F. Troiani (Modena) also contributed for quantum computation modeling.

5.1 Cr$_7$Ni as effective two-level system.

5.1.1 Magnetic characterization

As discussed more in general in Chapter 3, the tendency of $\chi T$-vs-$T$ is due to the antiferromagnetic Cr-Cr and Cr-Ni interaction (Fig. 5.1(a)). The room temperature value $\chi T \simeq 13$ emu K mol$^{-1}$ is close to the paramagnetic limit of seven Cr$^{3+}$ and one Ni$^{2+}$ uncoupled ions, at low temperature $\chi T(2 \text{ K}) \simeq 0.38$ emu K mol$^{-1}$, as it is expected by Curie law for a paramagnetic $S = 1/2$ state. The magneti-
Figure 5.1: (a) \( \chi_T \)-susceptibility of \( \text{Cr}_7\text{Ni} \) plotted as \( \chi_T \)-vs-\( T \). Measurements were taken with a 10 Oe ac field and frequencies 90, 1730, 9300 Hz on powders, evidencing no frequency dependence. Inset: Magnification of the low temperature region. The paramagnetic limit for \( S = 1/2 \) is indicated by dashes. (b) Magnetic field dependence of magnetization \( M \)-vs-\( H/T \). measured with a \text{dc} extraction magnetometer on powders (red markers). The blue markers display the \( M \)-vs-\( H/T \) measurement taken with an Hall probe magnetometer at \( T = 0.4 \) K (arbitrary units). Solid line curve represents a \( S = 1/2 \) Brillouin function plotted for comparison.

The specific heat \( C(T, H_0) \) of \( \text{Cr}_7\text{Ni} \) was measured as a function of temperature \( T \) and static magnetic field \( H_0 \) (Fig. 5.2(a)). Schottky anomaly at \( H_0 = 0 \) is related to the splitting of the ground state and not expected for a Kramers doublet (see Chapter 3). The curve taken for \( H = 0 \) exhibits a Schottky anomaly peaked at \( T \simeq 4 \) K which is related to the energy gap between the first excited and ground multiplets. Considering that the maximum of the Schottky anomaly

\[\text{The misalignment of the sample should be considered to obtain a better agreement.}\]
Figure 5.2: (a) Specific heat $C/R$ of a single $\text{Cr}_7\text{Ni}$ crystal as a function of the temperature ($T$) and of the magnetic field ($H_0$). The apparent slower decrease of the curve $C(T, H = 0)$ at $T < 1\,\text{K}$, was not fully reproducible and it was tentatively ascribed to spurious effects. (b) Torque signal measured on a 0.7x1x0.5 mm$^3$ $\text{Cr}_7\text{Ni}$ crystal at $T = 2\,\text{K}$ and $H_0 = 2\,\text{T}$. 
occurs at \( \simeq 0.4 \) times the energy gap, the latter results \( \Delta \simeq 10 \) K. Another Schottky anomaly is found at \( H_0 = 1 \) T and lower temperature \( (T \simeq 0.6 \) K\), whose maximum is shifted toward higher \( T \) for \( H_0 > 1 \) T. Having in mind the results of susceptibility and magnetization measurements, we can associate this anomaly to the splitting of the degeneracy of the ground doublet that creates an energy gap between the ground state \( |S = 1/2, M = -1/2 \rangle \) and the first excited state \( |S = 1/2, M = +1/2 \rangle \).

Torque magnetometry was employed to probe the axial anisotropy of \( \text{Cr}_7\text{Ni} \). The torque measurement \( \tau_y\)-vs-\( \theta \) was performed for \( H_0 = 1 \) T and \( T = 2 \) K and I just mention that no angular dependence of \( \tau_y \) was observed. In agreement with the \( M\)-vs-\( H_0 \) curve at \( T = 2.3 \) K (Fig. 5.1(b)), this result is due to the fact that for this temperature and magnetic field \( (H/T = 0.5 \) T/K\) only ground doublet is populated, which is unaffected by the anisotropy. Increasing the magnetic field \( (H_0 = 2 \) T\), higher-lying excited levels are populated and finite \( \tau_y\)-vs-\( \theta \) signal is observed (Fig. 5.2(b)). The sign of the sinusoid in correspondence to the principal directions \( \theta = 0^\circ, 90^\circ, 180^\circ \) and \( 270^\circ \) shows that the anisotropy of the multiplet under examination is easy-plane (see Section 2.2.3).

We get more quantitative informations by the diagonalization of the Hamiltonian \( \mathcal{H} \) (Eq. 1.5). The eigenstates \( \epsilon_i \) of \( \mathcal{H} \), together with Eq. 2.23, allow to calculate the magnetic contribution to the specific heat, while the lattice contribution is evaluated by means of Eq. 2.20. The best fit of the experimental data, which is reported in Fig. 5.2(a) by the solid lines, provides the following set of parameters: \( \Theta_D = (158 \pm 10) \) K, \( \delta = 0.42 \) K\(^{-1}\), \( J_{Cr}/k_B = 17 \) K, \( J_{Ni}/J_{Cr} = 0.9 \), \( |d_i|/k_B = 0.3 \pm 0.15 \) K (for all the spin sites), \( g_{Cr} = 1.98 \) and \( g_{Ni} = 2.20 \). The sign of \( d_i \) is obtained directly by the torque measurement in Fig. 5.2(b), which shows \( d_i < 0 \).

### 5.1.2 Discussion

**Pattern of the low-lying energy levels**

The energy spectrum calculated from the Heisenberg term of \( \mathcal{H} \) are shown in Fig. 5.3(a) as a function of the total spin \( S \). A parabolic band, formed by states with minimal energy for each \( S \) value, is easily identified. The levels belonging to
Cr$_7$Ni as effective two-level system.

Figure 5.3: (a) Energy spectrum of the Cr$_7$Ni molecule calculated from the isotropic term of Eq. 1.5. (b) Energy levels as a function of a static magnetic field applied along the z axis. At zero field the ground-state doublet is energetically well separated from the higher states ($\Delta \simeq 13$ K), thus representing a suitable choice for the qubit encoding.

this parabolic band have energies that closely follow the Landé rule. As discussed in Ref. [21, 22], these excitations are related to the combined quantum rotation of the oppositely oriented total spin on each Néel sublattice of the AF wheel. When we include in \( \mathcal{H} \) (Eq. 1.5) the microscopic parameters obtained from specific heat, we are able to draw the pattern of the low-lying energy levels \( \epsilon_i \) as a function of \( H_0 = H_0 \hat{z} \) (Fig. 5.3(b)). At zero field the ground state is a degenerate doublet \( (\epsilon_{0,1}) \), with a largely dominant (\( \gtrsim 99 \% \)) total-spin component \( S = 1/2 \); the first excited level is a quadruplet \( (\epsilon_{2-5}) \) \( S = 3/2 \) state belonging to the Landé band, with barycenter at \( \Delta \simeq 13 \) K. Noticeably enough, these low values of \( S \)-mixing allow us to consider the total spin as a good quantum number for the lowest eigenstates of the Cr$_7$Ni molecule.

In the perspective of processing of quantum information, the previous features of Cr$_7$Ni satisfy the necessary requirements. The first one is the energy difference between the ground-state doublet and the higher-lying levels, i.e., \( \Delta = \epsilon_2 - \epsilon_1 \): in fact, \( \Delta \) determines to which extent the ring behaves as an effective two-level system, i.e., a meaningful population of any state but \( |0\rangle \) and \( |1\rangle \) can be avoided throughout the molecule manipulation. The second one is the splitting between the two \( S = 1/2 \) states, \( \delta = \epsilon_1 - \epsilon_0 \): \( \delta \) fixes the temperature the system has to be cooled at in order to be initialized to its ground state. Likewise the same existence of a ground-state doublet and the suppression of the \( S \)-mixing, the large energy
separation from the higher states in the present molecule, $\Delta \simeq 13$ K, is a nontrivial result of the system engineering. Besides, the magnetic field allows a further tuning of the molecules level structure. In particular, it increases $\delta$, whereas it decreases the energy difference $\Delta(H_0)$ between $|1\rangle \simeq |S = 1/2, M = 1/2\rangle$, and $|2\rangle \simeq |S = 3/2, M = -3/2\rangle$. The achievement of the best trade off between the conflicting requirements of maximizing $\delta$ and $\Delta$ therefore determines the optimal value of the field, which it can be identified with $H_0 = 2$ T (see the discussion below). As a consequence, the achievable temperature required for the system initialization to the $|0\rangle$ state is $T \ll \delta/k_B \simeq 2.4$ K, whereas $\Delta \simeq \Delta(0) - 2g\mu_B H_0 \simeq 9.4$ K. On the ground of the above results, the Cr$_7$Ni molecule can be considered as an effective $S = 1/2$ spin cluster, and the information states $|0\rangle$ and $|1\rangle$ safely identified with its ground-state doublet.

**Dynamics**

The time simulation of the quantum gates provides an important feedback for the optimization of the physical parameters. The general unitary transformation applied to the computational space can be decomposed into a sequence of elementary gates, such as rotations of the single-qubit and the controlled $CNOT$ [132]. I start by considering the former, which can be obtained as a combination of three rotations about any two orthogonal axes, e.g., $U(\alpha, \beta, \gamma) = \exp(-i\alpha \sigma_y) \exp(-i\beta \sigma_x) \exp(-i\gamma \sigma_y)$, being $\sigma_{x,y}$ the Pauli matrixes. Transitions between the $|0\rangle$ and $|1\rangle$ states, i.e., rotations about the $x$ and $y$ axes, can be induced by means of resonant, in-plane electromagnetic pulses $H_1(t) \cos \omega t$, where $H_1(t) \ll H_0$ represents the slowly varying envelope. In the present case, however, the transverse magnetic field also couples the $|0\rangle$ and $|1\rangle$ states to the higher-lying ones, thus inducing a population loss (leakage) during gating, quantified by $L = 1 - [||\langle 0|\phi(t)\rangle|^2 + ||\langle 1|\phi(t)\rangle|^2]$. More specifically, the possible occurrence of such unwanted transitions is due to the $S$-mixing and to possible intrachannel inhomogeneities in the magnetic fields (or, equivalently, in the ion $g$ factors): both result in nonvanishing matrix elements $\langle 0, 1 |H_{\text{op}}| i \geq 2 \rangle$, with $H_{\text{op}} = \mu_B \sum_{i=1}^{8} g_i \mathbf{H}_1 \cdot \mathbf{s}_i$. Together with a molecular engineering aimed at the suppression of the $S$-mixing, the minimization of $L$ can be achieved by the use of soft enough pulses, i.e., by keeping the pulse spectral dispersion $\Delta \omega < (\Delta - \delta)/\hbar$. Being $\Delta \omega \sim 1/\tau_g$, such
Figure 5.4: Simulated time evolution of the molecular magnet, initially prepared in $|0\rangle$, under the effect of a transverse magnetic field with a Gaussian temporal profile. The black (solid), red (dashed), and blue (lower) lines correspond to $|c_0|^2$, $|c_1|^2$, and $L$ (multiplied by a factor $10^5$ in (a)), respectively; the static field is (a) $H_0 = 2$ T and (b) $H_0 = 5.61$ T, whereas $A = 0.1$ T in both cases.

inequality gives a lower bound to the ratio $\tau_g/\tau_d$ that can in principle be achieved ($\tau_{g,d}$ are the gating and decoherence time, respectively).

Here, by means of a numerical integration of the Schrödinger equation, the time dependence of $|c_{0,1}|^2 = |\langle 0,1|\Phi(t)\rangle|^2$ is calculated and of $L$ corresponding to a $\pi$, rotation about the $x$ axis, for $|\Phi(0)\rangle = |0\rangle$ and $H_0 = 2$ T (see Fig.5.4(a)); the pulsed field is assumed to have a Gaussian profile $B_1 = A \exp[-(t-t_0)^2/(2\sigma^2)]$, with $A = 0.1$ T and $\sigma = 150$ ps. To a very large extent the leakage involves the first excited multiplet, and its value remains lower than $10^{-5}$ throughout the time evolution. Further simulations, performed with more reasonable values of the magnetic field ($A = 0.01$ T) [44], give proportional increases of the pulse duration, with a further suppression of $L$. We have also investigated the gate robustness with respect to possible spatial inhomogeneities of $H_1$, generally leading to a larger value of $L$: even in the worst limiting case of a $H_1$ which is nonzero only at the Ni-ion site, $L$ remains below the threshold of $10^{-4}$ ($A = 0.15$ T, $\tau_g \sim 2\sigma \sim 300$ ps).
Decoherence

Decoherence is related to the possible entanglement between the system, described by \( H \) (Eq. 1.5), and the environment. Such phenomenon, lies at the heart of the quantum-classical transition and of the measurement problem. Decoherence also represents a key issue from a technological point of view, because the condition \( \tau_d \gg \tau_g \) is a necessary requirement for deploying the processing of the quantum information.

On the ground of simply considerations on dipolar interaction, the decoherence is expected to mainly arise from the hyperfine coupling with the nuclear spins. A first estimate can be obtained by considering the dipolar interaction of one Cr ion \((s = 3/2)\) with the neighboring F nucleus (natural abundance \(\sim 100\%\) of the \(I = 1/2\) isotope). Being \(g_F = +5.2577\) and the distance of each of the 8 F atoms from the nearest Cr ion \(d = 1.91\) Å, the interaction energy corresponds to \(E_{hyp}/k_B = 0.38\) mK. For an octanuclear ring this would give \(\tau_d \simeq \frac{\hbar}{8E_{hyp}} \sim 2.5\) ns, that can be considered as a lower bound for \(\tau_d\). Similar \(\tau_d\) values have been estimated for other molecular magnets [133, 134].

A second potential source of decoherence, the ring-ring dipolar coupling, is characterized by a lower energy scale, \(E_{dip}/k_B \simeq (g\mu_B S)^2 \sim 0.1\) mK \((S = 1/2\) and \(V = 6346\) Å\(^3\)), further reducible in diluted Cr\(_7\)Ni molecular arrays or crystals.

The key-role of the decoherence mechanism is stimulating intense experimental activity in order to quantify directly \(\tau_d\). In Ref. [135] Wernsdorfer et al. measured the electron-spin resonance linewidth by means of magnetization measurements with resonant photon absorption. Their results, which also include the effects of possible inhomogeneities, the so-called dephasing, indicates a lower bound of \(\tau_d \simeq 25\) ns. More recently, Ardavan et al. (Ref. [136]) used pulsed electron-spin resonance (spin echo) experiments to show that the relaxation and decoherence times in Cr\(_7\)Ni are significantly longer than the duration of the coherent manipulation. The \(\tau_d\) time evaluated in this reference exceeds the expectations of Ref. [135] (worst-case) by 3 orders of magnitude, reaching 0.55 \(\mu s\) at 1.8 K, and 3.8 \(\mu s\) for the perdeuterated analogue, obtained substituting \(^1\)H with \(^2\)D nuclei. They indeed found that the phase-coherence is dominated by the coupling to the nuclear moments of protons in the vicinity of the cluster, while they report no evidence of coupling between the magnetic cluster and the fluorine nuclei. On
the other hand, in Ref. [137], Micotti et al. show that the pronounced broadening and structure of the $^{19}$F NMR spectrum in Cr$_7$Cd is the result of the hyperfine interactions with the Cr$^3$ moments.

In other to shed the light on such apparently discording results, Troiani et al. (Ref. [138]) theoretically investigated the effect of hyperfine interactions on the electronic coherence of a single Cr$_7$Ni molecule. They distinguished two mechanisms of decoherence, the first acts on the time-scale of $\sim 10$ ns is due to local fluctuations of the nuclear environment; the second, and major one, is due to Cr, H and F nuclei, that are mainly responsible for the average electron-nuclear entanglement, with a rate $0.1 \, \mu s^{-1}$. The electron coherence can be partially recovered by applying suitable spin-echo sequence, that leads to cancellation of both effects, giving explanation to the experimental results in Ref. [136].

The identification of coupling to the H and F nuclei as the main decoherence path offers a strategy for synthesizing structures with even better coherence properties by reducing as far as possible their number in the vicinity of the cluster.

### 5.1.3 Conclusions

In conclusion, the energy spectrum of the investigated Cr$_7$Ni molecule fully justifies its description in terms of an effective two-level system; besides, the symmetries of the ground-state doublet ($S$-mixing below 1%) suppress the coupling to the higher levels as induced by the transverse magnetic fields which are required for the quantum-gate implementation. In fact, our simulations of the single-qubit gates provide negligible values for the leakage ($L \lesssim 10^{-4}$) even for gating times of the order of $10^3$ ps. The $3 \, \mu s$ (Ref. [136]) estimated for the spin decoherence times is well below the state-of-art time scale of instrumentation for coherent manipulations of the electron spin ($10$ ns). While further work is needed for the engineering of the intercluster coupling, our results paved the way to use Cr$_7$Ni wheels for the qubit encoding and manipulation.
5. Antiferromagnetic molecular rings for quantum computation

Figure 5.5: Structure of Cr$_9$Ni. Colors: Cr, green; Ni, pale blue; Zn, orange; F, yellow; O, red; C, black; N, blue. H-atoms omitted for clarity.

5.2 A class of two-levels systems: the Cr$_9$Ni ring

The structure of Cr$_7$Ni can be replied by choosing a proper secondary amine to obtain cores with different nuclearity. Cr$_8$Ni was produced (Ref. [125]), which shows characteristics dissimilar to Cr$_7$Ni and frustrated ground state. Ref. [123] reports the synthesis of decametallic wheels, showing few derivatives with different structures. Hereafter I will refer only to the most symmetric Cr$_9$Ni ring, namely

$$[\text{H}_2\text{NtBuisPr}][\text{Cr}_9\text{NiF}_{10}(\text{O}_2\text{CCMe}_3)_{20}],$$

which is displayed on Fig. 5.5. The preliminary characterization shows indeed that the other clusters have ellipsoidal structure and ground state $S_0 \neq 1/2$ [123].

The temperature dependence of the ac susceptibility $\chi_T$-vs-$T$ of Cr$_9$Ni is plotted in Fig. 5.6(a). At high temperature, $\chi_T$ tends to saturate to 17.5 emu K mol$^{-1}$ quite close to the paramagnetic limit expected for 9 uncoupled spins $s = 3/2$ plus one $s = 1$. At low temperature, $\chi_T$ points to 0.38 emu K mol$^{-1}$, suggesting $S = 1/2$ ground state. Specific heat (Fig. 5.6(b)), similarly to Fig. 5.2(a) shows vanishing zero-field-splitting as expected for a ground state doublet.

The energy levels are calculated by the diagonalization of Eq. 1.5, and the microscopic parameters are determined by fitting the experimental data of susceptibility $\chi(T)$ and specific heat $C(T, H)$ (Fig. 5.6). The set of parameters that
A class of two-levels systems: the Cr$_9$Ni ring

Figure 5.6: (a) The product of ac-susceptibility $\chi$ and temperature $T$, $\chi T$, of Cr$_9$Ni as a function of the temperature $T$. Inset: enlargement at low temperature. Extrapolation of $\chi T$ for $T = 0$ gives 0.38 emu K mol$^{-1}$. (b) Specific heat normalized to the gas constant $R$, $C/R$ of Cr$_9$Ni as a function of the temperature ($T$) measured at different the magnetic field ($H$). Calculations are represented with the solid lines.

Figure 5.7: Pattern of the spin levels of Cr$_9$Ni calculated after the diagonalization of the exchange term of the Hamiltonian operator.
better reproduces the experimental data is $J_{Cr}/k_B = 15.8 \pm 0.8$ K, $J_{Ni}/J_{Cr} = 1.1 \pm 0.1$, $|d_i|/k_B = 0.3 \pm 0.2$ K, $g_{Ni} = 2.1 \pm 0.1$ and $g_{Cr} = 2.0 \pm 0.1$ (simply $g_{Ni} = g_{Cr} = g = 2.1$ for the fit of $\chi(T)$). These values are quite close to those found for Cr$_7$Ni and this is not surprising since the bridging units between metals are essentially the same in these derivatives.

The pattern of energy levels is depicted in Fig. 5.7 and it turns out that the ground state is an $S = 1/2$ doublet, the first excited state is an $S = 3/2$ quartet then higher excited states are present. Because of the $1/n$ scaling factor of the rotational band levels [20], the energy gap between the ground and the first excited multiplets results lower in the Cr$_9$Ni molecule ($n = 10$) respect than Cr$_7$Ni ($n = 8$). When the zero-field splitting of the $S = 3/2$ is considered, the gap results $\Delta \simeq 8$ K, therefore smaller than Cr$_7$Ni ($\Delta \simeq 13$ K). This value that may induce non-negligible leakage population outside of the $S = 1/2$ doublet, which is very small in Cr$_7$Ni (see Section 5.1.2), but is more relevant in Cr$_9$Ni.

In conclusion, a class of antiferromagnetic wheels Cr$_n$Ni with $n = 7, 8, 9$ was synthesized templating the structure of Cr$_7$M. The magnetic properties of the Cr$_9$Ni cluster results similar to Cr$_7$Ni , having features suitable for quantum information processing.
5.3 Entanglement on linked Cr$_7$Ni complexes

In Ref. [139] Affronte et al. reported the supramolecular fabrication of molecular dimers of Cr$_7$Ni, which are linked by means of diamines H-bonded onto the ring cavity. The same concepts have been recently proposed for polyoxometallates, as described in Ref. [140]. Several amines can work as linker, the magnetic characterization showed that the Cr$_7$Ni properties are preserved, whereas the correlation resulted too weak to be appreciated for $T \geq 0.4$ K.

Others linked Cr$_7$Ni complexes were synthesized and they are reported in Ref. [41, 141, 142]. In Fig. 5.8 is depicted the structure of

$$\text{C}_{216}\text{H}_{301}\text{CoCr}_7\text{F}_8\text{N}_{10}\text{NiO}_{40},$$

CoPc-Cr$_7$Ni in short, where a Cr$_7$Ni cluster is linked to a Co phthalocyanine (C$_{128}$H$_{144}$N$_8$O$_8$Co). Following Ref. [139], the amine is H-bonded to F atoms onto the ring cavity. This system is drawn to put in practice the idea of a simple control spin (CoPc) coupled to a more complex molecular cluster (Cr$_7$Ni). Furthermore, the shorter path between Cr$_7$Ni and CoPc may allow a stronger
interaction between the magnetic centers.

Specific heat of CoPc-Cr$_7$Ni is shown in Fig. 5.9, where the $C(T, H)$ data of Cr$_7$Ni multiplied by a factor 2 is also reported for comparison. The two sets of data roughly show the same behavior. For $T < 1$ K, $C(T, H = 0)$ of CoPc-Cr$_7$Ni does not show any extra Schottky anomaly, which is expected when the exchange coupling set in. This observation should therefore rule out the possible existence of correlated states in this temperature range. The H-bond can establish the exchange path only if it is accompanied by a substantial overlap of the atomic orbitals [45], which probably lacks between F atoms and amine group. The discrepancies between the curves arise just because of the different lattice contribution and energy level spectrum of Cr$_7$Ni and CoPc.

In Ref. [139], the problem of the switchability of the linkers was also explored. To illustrate the possibility to insert a switch onto the linker, (Cr$_7$Ni)$_2$M$_2$ ($M = Cu, Ni, Co$) complexes were synthesized, where the $M_2$ dimer is enclosed in between the two linking amines. The idea they pursued is that the state of the dimer might open ($S = 0$) or close ($S \neq 0$) the exchange path. Similar systems
Entanglement on linked Cr$_7$Ni complexes

Figure 5.10: Molecular structure of (Cr$_7$Ni)$_2M$, where $M = $ Cu. Color scheme: Cr/Ni disordered within the wheel: green, Cu: large black ball, F: yellow, O: red, C: small black ball, N: blue. Selected bond lengths (Å). For $M = $ Cu: Cu-O (NO$_3$) 2.10, Cu-O (NO$_3$) 1.96, Cu-N (Py) 2.02, Cu-N (Py) 2.04, Cu-O (O=CM$_2$) 2.361. For $M = $ Ni: Ni-O (NO$_3$) 2.08, Ni-O (NO$_3$) 2.05, Ni-N (Py) 2.11, Ni-N (Py) 2.11, Ni-O (H$_2$O) 2.17, Ni-O (H$_2$O) 2.08.

Figure 5.11: Molecular structure of (Cr$_7$Ni)$_2$Ru$_2$BF$_4$. Color scheme: Cr/Ni disordered within the wheel: green, O: red, F: yellow, C: small black ball, N: blue, Ru: large orange ball, Me groups on rings and on dimer have been omitted for clarity, BF$_4$ not shown. Selected bond lengths (Å): Ru-Ru 2.274, Ru-N (Py) 2.33.
that I investigated are (Cr\textsubscript{7}Ni\textsubscript{2}Cu and (Cr\textsubscript{7}Ni\textsubscript{2}Ni, which were realized using a single metal instead of a dimer to simulate the case in which the interaction is always on [41]. For these systems, I just mention that magnetic characterization indicates that the coupling is too weak to be sizable down to $T \sim 0.3$ K.

A prototype of molecular switch via redox reaction is found in the ruthenium Ru\textsuperscript{2+}Ru\textsuperscript{3+} dimer which has two accessible oxidation states [143]. Its magnetic characteristics are expected to change when an electron is injected in the linker. Super-complexes have been synthesized where a ruthenium dimer Ru\textsubscript{2}Piv\textsubscript{4}BF\textsubscript{4} is suitably functionalized with amines to bond two Cr\textsubscript{7}Ni: the result

\[
\{\text{Ru}_2(O_2C\text{CMe}_3)_4\text{BF}_4\}\{[\text{PyCH}_2\text{NH}_2\text{Et}]\text{[Cr}_7\text{NiF}_8(O_2C\text{CMe}_3)_{16}]\}_2,
\]

hereafter shortly named as (Cr\textsubscript{7}Ni\textsubscript{2}Ru\textsubscript{2}Piv\textsubscript{4}BF\textsubscript{4}, is displayed in Fig. 5.11. Susceptibility (Fig. 5.12) does not show clear deviations from the expected for two isolated Cr\textsubscript{7}Ni wheels and the Ru\textsuperscript{2+}Ru\textsuperscript{3+} dimer. This is confirmed by low temperature specific heat measurements (Inset of Fig. 5.12) which do not reveal any evidence of low-energy interaction except for the energy gap between the $S = 1/2$ and the $S = 3/2$ first excited state of the Cr\textsubscript{7}Ni molecular clusters.
Figure 5.13: (a) Temperature dependence of the $\chi T$ product for the (Cr$_7$Ni)$_2$Ru$_2$Piv$_4$PF$_6$ derivative as compared with that of bare Ru$_2$Piv$_4$PF$_6$ dimer and twice that of Cr$_7$Ni. Inset: low-temperature behavior. (b) Low-temperature specific heat, normalized to the gas constant $R$, of (Cr$_7$Ni)$_2$Ru$_2$Piv$_4$PF$_6$ derivative as compared with that of bare Ru$_2$Piv$_4$PF$_6$ dimer and twice that of Cr$_7$Ni. Arrows indicate the Schottky anomalies.

More recently, Ru$_2$Piv$_4$PF$_6$ instead of Ru$_2$Piv$_4$BF$_4$ has been used as starting product for the synthesis of (Cr$_7$Ni)$_2$Ru$_2$Piv$_4$PF$_6$, namely

\[
\{\text{Ru}_2(\text{O}_2\text{CCMe}_3)_4\text{PF}_6\}\{\text{PyCH}_2\text{NH}_2\text{Et}[\text{Cr}_7\text{NiF}_8(\text{O}_2\text{CCMe}_3)_{16}]\}\_2,
\]

which has the same structure of Fig. 5.11. In Fig. 5.13(a) I report the temperature dependence of the $\chi T$ product for (Cr$_7$Ni)$_2$Ru$_2$Piv$_4$PF$_6$, which is compared to the $\chi T$ value measured on the starting Ru$_2$Piv$_4$PF$_6$ dried powders and with twice the $\chi T$ value measured on simple ring Cr$_7$Ni. The $\chi T$ for bare Ru$_2$Piv$_4$PF$_6$ dimer shows weak temperature dependence and it tends to saturate to 1.3 emu K/mol at low temperature, that is compatible with an $S = 1$ ground state for the Ru dimer. The $\chi T$ product for the (Cr$_7$Ni)$_2$Ru$_2$Piv$_4$PF$_6$ derivative turns out to be quite close to the sum of the two contributions from the Cr$_7$Ni and the Ru$_2$Piv$_4$PF$_6$ dimers in the whole temperature range down to 2 K (see inset of Fig. 5.13). This demonstrates that the supramolecular synthesis essentially preserve the main features of the starting molecular blocks. Weak interactions are expected at lower temperatures. To check this point we have studied the low-temperature behavior of the specific heat in the three derivatives (Fig. 5.13(b)).
5. Antiferromagnetic molecular rings for quantum computation

![Molecular structure of (Cr7Ni)2Cu2](image)

**Figure 5.14:** Molecular structure of (Cr7Ni)2Cu2. Color scheme: Cr: pink, Ni: orange, Cu: blue, F: green, O: red, C: small black ball, N: blue. tBu and (C3H7)2NH2 groups on rings and on dimer have been omitted for clarity.

The $C(T, H)$ of Ru2Piv4PF6 dried powders shows a Schottky anomaly centered at 0.3 K, whose origin is probably due to the splitting of the ground state. Interestingly, a Schottky anomaly centered at 1 K is observed in the $C(T)$ data of (Cr7Ni)2Ru2Piv4PF6 derivative. This indicates that an excitation of the order of one or few Kelvin is present in this compound, differently to what observed for the original derivatives. It is likely that the splitting of the ground state of the Ru2Piv4PF6 dimer is modified when this group is inserted in the supramolecular structure, and consequently the Schottky anomaly is lifted to higher temperature. States and levels of the two Cr7Ni rings can also be involved and contribute to this anomaly. This is an interesting possibility since it would imply that states of Cr7Ni rings could be linked in some way through the Ru dimer that, in turn, can be switched by an external electrical stimulus.

Nevertheless, further work is needed to prove the effectiveness of the magnetic coupling between two molecular Cr7Ni rings and the switchability of the Ru2+Ru3+ dimers.

Recently, new complexes were synthesized, which are especially drawn to re-
Figure 5.15: (a) Temperature dependence of the $\chi T$ product for the (Cr$_7$Ni)$_2$Cu$_2$ derivative as compared with twice that of Cr$_7$Ni. The shift of the curves is probably related to diamagnetic contributions. (b) Low-temperature specific heat, normalized to the gas constant $R$, of (Cr$_7$Ni)$_2$Cu$_2$ derivative as compared with twice that of Cr$_7$Ni.

The molecular structure of

$$[(C_3H_7)_2NH_2Cr_7NiF_8(O_2CCMe_3)_{15}(O_2CC_5H_4N)]_2Cu_2(O_2CCMe_3)_{24},$$

in short (Cr$_7$Ni)$_2$Cu$_2$, is depicted in Fig. 5.14. The linking path between the two clusters of Cr$_7$Ni is made by the Cu$^{2+}$ dimer and diamine, which is directly bonded to the carboxilate bridge between Cr$^{3+}$ and Ni$^{2+}$ metals to substitute the pivalate group.

Preliminary characterization by means of ac-susceptibility (Fig. 5.15(a)) and specific heat (panel (b)), shows that the properties of Cr$_7$Ni are preserved. No coupling effects are evidenced. Regardless, this behavior was expected because the dimer should lie in the $S = 0$ ground state, that breaks the potential exchange path. Additional measurements on the isolated Cu$^{2+}$ dimer should clarify its behavior and prove the effectiveness of the linking mechanism.
5. Antiferromagnetic molecular rings for quantum computation
Chapter 6

SHPM imaging of magnetic domains

In this Chapter I present the results I obtained by SHPM in the study of the magnetic domains in Ba-ferrite single-crystals. The aim of this work was twofold: on the one hand, to test the new SHPM microscope on a well-known system such as ferrite. On the other hand, we wanted to investigate the evolution of the domain branching under applied-field by a novel technique.

This work was done in collaboration with Dr. F. Albertini and Dr. F. Licci (CNR-IMEM Parma) for crystal growth and data analysis respectively.

6.1 Domain branching in ferrite crystals

6.1.1 Domain branching

Domain branching consists in the progressive refinement, by iterated generation of smaller domains, of the bulk domains towards the surface (see Fig. 6.2). Ferrite magnets have been studied since the 1960 for applications such as permanent magnets and data-recording on tape. The magnetization loop of ferrite crystals shows characteristic butterfly-like shape, and it is accounted by the competition between stripe and bubble domains. Early studies of domain pattern shape was performed by Bitter and Faraday techniques [63].

When the crystal thickness is large enough ($t \simeq 100 \mu$m), the shape of the
6. SHPM imaging of magnetic domains

Figure 6.1: Bulk magnetization of the BaFe$_{12}$O$_{19}$ single crystal measured at different temperatures by means of the dc-extraction technique. The magnetic field is applied along the easy axis of the magnetization.

surface domains tends to minimize the magnetostatic energy, thus leading to very complex and beautiful patterns [63]. This phenomenon is known as domain branching and it is typical of materials that present high ratio between magnetocrystalline and shape anisotropy ($\beta = K/K_d \gg 4\pi$).

This domain branching has recently drawn a renewed interest for the study of high performance permanent magnets [145] and electron transport in magnetic nanostructures [144]. Kooy and Enz [146] and Cape and Lehman [147] developed theoretical models to explain the experimental results. In Ref. [144], Minyukov and García report a theoretical model which describes the evolution of the branched domains upon applied-field. We utilize SHPM to investigate the domain pattern at surface of a 150 $\mu$m thick single crystal of Ba ferrite. Our in-field measurements show agreement with the predicted behavior.

6.1.2 Experiments

We studied a BaFe$_{12}$O$_{19}$ single crystal with hexagonal structure, that was prepared by slowly cooling a supersaturated solution (PbO flux) from 1150 $^\circ$C to room temperature [148]. The crystal was a platelet (thickness $t = 150 \mu$m, area $\approx 4 \times 6$ mm$^2$) having the largest face normal to the crystallographic c-axis. The sample was polished and coated with a gold layer (thickness 25 nm) to obtain a
Figure 6.2: (a) Room temperature SHPM image taken at the surface of a $t=150 \mu m$ thick BaFe$_{12}$O$_{19}$ single crystal in zero applied magnetic field. The inspected crystal face is normal to the crystallographic $c$-axis and the area represented is $56 \times 56 \mu m^2$. The height of the Hall sensor with respect to the surface is $h \approx 450$ nm and the image is taken in the lift mode (no feedback). (b) The same area of (a) scanned with the Hall probe at a distance of $h \approx 250$ nm from the sample in the tunneling mode. The yellow color corresponds to "outgoing" stray fields (i.e. magnetic field coming out from the sample's surface towards the Hall probe) while the black one represent the "incoming" field. The zero-field value of the scale is set to an arbitrary baseline. The magnetic signal spans $\approx 2700$ Oe for $h = 250$ nm, and $650$ Oe for $h = 450$ nm.

6.1.3 Results

Bulk magnetization loop

Fig. 6.1 shows the magnetization $M$-vs-$H$ of the bulk crystal, which was measured by the dc-magnetometer applying the magnetic field orthogonally to the surface. At room temperature, $M$ linearly increases from the demagnetized state up to $H_1 \approx 3100$ Oe, where the slope progressively decreases to saturate for $H = H_2 \approx 4100$ Oe. Reversing the field direction, the saturation persists beyond $H_2$ to the nucleation field $H = H^*$, where $M$ suddenly drops to $H \approx H_1$ thus closing the hysteresis loop in the first quadrant of the $M$-vs-$H$ loop. The magnetization at the
saturation is $M_s = 385$ G. Lowering the temperature, the $M$-vs-$H$ curves display similar shapes whereas the value of both $M_s$ and $H_2$ increase ($M_s(5 \, \text{K}) = 538$ G and $H_2(5 \, \text{K}) = 6100$ G).

**SHPM imaging**

The Hall probe detects the stray field $B_{sf}$ of the sample’s surface. The intensity and profile of $B$ changes with the distance, hence the separation between the Hall sensor and the surface (height $h$), influences the features of the profile. Fig. 6.2 displays a comparison between an image taken in the lift mode (Panel (a), $h \approx 450$ nm) and one taken in the tunneling mode (Panel (b), $h \approx 250$ nm). The intensity of the detected magnetic flux $B_{sf}$ is represented by the graduate color scale: yellow indicates the maximum value of $B_{sf}$ whereas black represents the minimum. In other words, the yellow spots corresponds to the stray field outgoing from the sample surface, while black color represents the incoming one. As expected, the images taken in tunneling mode (Fig. 6.2(b)) reveals more details than in the lift mode (Fig. 6.2(a)), thus clearly evidencing the role of the Hall probe height.

Fig. 6.2(b) shows the details of the domain pattern. Both yellow and black stripes show corrugated boundaries and contain (red) inclusions of reversed magnetic field with irregular shape. This structures are characteristic for domain branching. The (mean) domain width can be defined as the ratio between a test area and the total domain wall length in this frame. One procedure of evaluating the domain width is based on a stereological method, described in Ref. [63], that consist in evaluate the number of intersection of the domain walls with an arbitrary test line. The result obtained with Fig. 6.2(b) is $w = 10 \, \mu\text{m}$.

The inclusions displayed in Fig. 6.2(b) can be divided in two sets according to their size. The bigger ones have $\sim 3 - 4 \, \mu\text{m}$ width, while the smaller ones have $\sim 1 \, \mu\text{m}$ width. The big inclusions are positioned in the middle of a stripe and they are surrounded by the others. The sequence of Fig. 6.3 taken at different applied field $H$, shows that the main features of domains essentially persist at low field; it is indeed possible to distinguish between the behavior of the stripe domains and the reversed inclusions generated by the branching up to 2 kOe. The application of an external magnetic field leads to an expansion of the yellow stripes
Figure 6.3: (a-n) The same area of Fig. 6.2 measured applying the external magnetic field $H$ perpendicularly to the sample’s surface. For each image, the color scale is chosen to cover the full data range.
6. SHPM imaging of magnetic domains

(i.e. magnetization parallel to the field direction) at the expenses of others, the black stripes, that progressively shrink (Fig. 6.3(e)). At $H > 3$ kOe (Fig. 6.3(g)) transition to bubble configuration can be observed and, finally, for $H > H_2$ the domain pattern gets full saturated in the field direction (Fig. 6.3(h)).

The external field also controls the evolution of the domain branching: the number of reversed inclusions in the black stripes progressively diminishes up to $H = 2000$ Oe, where the smallest inclusions disappear (Fig. 6.3(d)). This reflects to the decrease of the generation number $s$ (see Ref. [144]). On the other hand, the reversed inclusions in the yellow stripes seem to gain intensity (Fig. 6.3(d)) and they persist until the full transition to the bubble configuration occurs (Fig. 6.3(g)). The corrugation of the domain boundaries progressively decreases (Fig. 6.3(d-e)) and they finally get completely smooth (Fig. 6.3(f)).

For decreasing field, accordingly to the bulk magnetization (Fig. 6.1), the saturation persists down to $H = H^*$, where the domains suddenly appear with stripes already reshaped by the branching effect (Fig. 6.3(h-k)). At $H = 0$ (Fig. 6.3(n)), the domain pattern is qualitatively similar to the demagnetized state but a smaller number of generations can be observed (lack of the red inclusions in the black stripes, and lack of the small inclusions in the yellow stripes). The sequence shows remarkable differences in the images at corresponding fields, as it is indeed expected by the strong magnetic-history dependence of these systems [63]. It is also worth noting that at corresponding fields (e.g. $H = 2000$ Oe) the domain configuration is more refined coming from saturation than from remanent state.

In Fig. 6.4(a-s) the images obtained in the lift mode, i.e. by scanning the head at a fixed height of 400 nm, are reported for comparison. In spite of the minor resolution, some information can still be evaluated. In the demagnetized state (Fig. 6.4(a)) bended and branched stripes have an average size $w=14$ µm, while as expected, when a magnetic field is applied ($H < H_1$ Fig. 6.4(b-d)), the area of the yellow domains increases at expenses of the black ones. Reached $H = H_1$, the width of the reversed domains remains constant while their length starts to decrease (Fig. 6.4(e-i)), and finally collapse to bubble domains at $H = 3600$ Oe (Fig. 6.4(i,j)), in agreement with Ref. [146]. At $H > 3700$ Oe the surface appears almost saturated (Fig. 6.4(k-l)). Decreasing the field, accordingly with the magnetization cycle, the domains remain saturated down to $H = H^*$ (Fig. 6.4(m))
Figure 6.4: (a-s) Room temperature SHPM images obtained scanning the Hall sensor in the lift mode at different magnetic fields. The area of the images is 56x56 $\mu m^2$. (t) Local magnetization curve measured during the field sweeping above the area in bottom-left corner of the image. The markers represent the mean signal of the 56x56 $\mu m^2$ region.
when, suddenly, stripe domains appear (Fig. 6.4(n)): they are initially straight but get bended as soon as the field decreases (Fig. 6.4(o-s)).

Fig. 6.5 shows a measurement taken $T = 5$ K with the same procedure of Fig. 6.4, thus demonstrating that the SHPM works well even at low temperature. In this conditions, the scanning area of the piezotube shrinks down to 5x5 µm, so, while it is still possible to acquire the surface magnetic contrast, the limited area of the image doesn’t allow to resolve the domain pattern features.

**SHPM local magnetization**

An alternative and complementary way to use Hall probe is to fix it on one specific point of the surface and use it as micro-magnetometer to probe local magnetization. In Fig. 6.4(a-s) a sequence of images is taken at fixed $H$. Fig. 6.4(t) shows the local magnetization picked up above the bottom-left corner during the sweep of the magnetic field (solid line). The curve reproduces well the shape of bulk measurement and the value of $H_1$, $H_2$ and $H^*$ as well. In Fig. 6.4(t) the markers represent the mean intensity of the signal of each image. The discrepancies between these points and the solid lines arise because of the domains and their local field. At $H = 0$, for instance, the line is beneath the marker. In Fig. 6.4(a), indeed, the probe is positioned above a dark domain sensing a signal lower than the mean-field of the image. Likewise, in the range $3100 < H < 3500$ Oe the magnetization locally decreases because a black domain move under the Hall probe (Fig. 6.4(e-h)). Similar arguments are valid also for the measurements at $T = 5$ K (Fig. 6.5).

**6.1.4 Discussion**

The $M$-vs-$H$ cycle of Fig. 6.1 is very similar to those reported by Kooy and Enz [146] and by Cape and Lehman [147] for BaFe$_{12}$O$_{19}$ platelets with thickness of few µm. All these $M$-vs-$H$ curves are characterized by saturation fields much smaller than $4\pi M_s$ and by a nucleation fields $H^* > 0$. The evolution of the domain pattern also follows the typical behavior: the width of domains with outgoing field increases at low applied fields, while close to saturation the reversed domains diminish their lenght and shrink to bubbles (cylindrical domains) before
The branching phenomenon is expected to appear at a characteristic thickness $D_s$, fragmenting and reducing the width of the domains in a number $s$ of generations. The value of $D_s$ can be evaluated following Ref. [63] and the result is $D_s = 23 \, \mu m$ in our case. The observation of the domain branching in our experiments (Fig. 6.2(b)) are thus justified because $t > D_s$. The evolution upon application of $H$ along the easy direction is discussed in Ref. [144] using a simplified model that consider a regular two-dimensional branching. If we indicate with $w_s$ the domain width of the $s$-th generation, and $w_0$ the width of the bulk domains, the model predicts that the ratio $w_s/w_0$ at $H/4\pi M_s = 0.4$ is twice respect to the case with $H = 0$. This fact has as consequence that the number of generations decreases to $s - 1$ at $H = 0.4 \cdot 4\pi M_s \simeq 2000 \, Oe$, in agreement with the observation of Fig. 6.3(d).

6.1.5 Conclusions

In conclusion, we investigated a thick Ba ferrite single crystal by means of SHPM, exploiting the capability of this tool to allow imaging and magnetization measurements upon the application of magnetic fields. We evidenced that the domain
6. SHPM imaging of magnetic domains

pattern of the sample is affected by the branching effect, in agreement with surface and bulk measurements obtained with different techniques and the theory.
Chapter 7

Prussian blue analogs
nanoparticles at surface

This Chapter is devoted to the study of the Prussian blue analogs nanoparticles. After introducing the magnetic properties of these systems (Section 7.1), I discuss their grafting on SiO$_x$ and SHPM magnetic characterization (Section 7.2).

This work was carried out with the contribution of T. Mallah and his group (synthesis, Orsay) and G. C. Gazzadi (FIB lithography, Modena).

7.1 Magnetic properties of PBA nanoparticles

In Ref. [150] Brinzei et al. describe the synthesis of (NiCr)-PBA nanoparticles having 6 nm size, that show narrow distribution and preserve the same structure of bulk PBA. These systems offer flexibility of functionalization are are suitable to be grafted at surfaces. Besides, diluted samples, in which the degree of the concentration can be controlled thus eventually modifying the strength of the interaction among the particles, were prepared. For this purpose a polymeric matrix of polyvinylpyrrolidone (PVP) has been successfully employed.

Bulk (NiCr)-PBA shows ferromagnetic transition at $T \simeq 70$ K (Section 1.1.4). Figure 7.1(a), shows the out-of-phase susceptibility $\chi''$-vs-$T$ of PBA nanoparticles diluted in PVP to 10%. The strongly frequency-dependency of $\chi''$, likewise Figure 7.1(a), can be associated to superparamagnetism. Nevertheless, the slowing down of the dynamics at the lowest temperatures ($\chi''$ is unaffected by the
Figure 7.1: Temperature dependence of the out-of-phase susceptibility at different ac-frequencies, as labeled, for (a) 10% and (b) 1% dilution of nanoparticles embedded in PVP.

Figure 7.2: Semi-logarithmic plot of the relaxation times respect to $T^{-1}$. The line represents the Arrhenius law for $E_a = 52$ K and $\tau_0 = 2 \times 10^{-8}$ s.
frequency change below \(\approx 4\) K) and the frequency-dependence of the maximum absorption, like those observed in Fig. 7.1 suggest the presence of inter-particle interactions \([151]\), that seems to be non-negligible even for sample with 1% concentration. While exchange paths are suppressed by the coating of the particles with PVP, dipolar interactions are indeed large, especially considering the very strong magnetic moment carried by each particle (\(\approx 2 \times 10^3 \mu_B\)).

To probe the single-particle dynamic, more diluted samples are needed where inter-particle interactions are reduced by the large spacing. Fig. 7.1(b) shows the out-of-phase susceptibility for 1 % (NiCr)-PBA in PVP. The behavior of \(\chi''\)-vs-\(T\) at low temperature evidence that the correlations are now notably weakened, even still non-completely suppressed.

For the 1% dilution of nanoparticles in PVP, the spin-lattice relaxation times (\(\tau\)) can be calculated by the maxima of the out-of-phase susceptibility (see Section 2.2.1), obtaining \(\tau = 0.1\) s at \(T = 3.4\) K (Fig. 7.2). The dependency respect to \(T\) is given by the Arrhenius law (Eq. 2.12); in the semi-logarithmic plot of Fig. 7.2 the fit of \(\tau\)-vs-\(T^{-1}\) allows to determine the characteristic activation energy, \(E_a \approx 52\) K, and the pre-exponential factor, \(\tau_0 \approx 2 \times 10^{-8}\) s.
### 7.2 PBA nanoparticles at surface

#### 7.2.1 Selective grafting by FIB-direct lithography

The grafting of the PBA nanoparticles on the silicon surface was carried out by a three-step procedure [154]: (1) functionalization of a H-terminated Si(100) substrate by undecanoic acid following a well-known procedure [155], (2) the acid terminated substrate was modified to obtain a dangling tridentate ligand that is able to chelate a Ni(II) metal ion, (3) a simple immersion of the substrate in an aqueous solution containing the nanoparticles allowed to obtain the grafted monolayer. Between step (2) and (3), I used FIB patterning to remove the organic ligand from selected regions of the substrate. I employed a FIB-SEM dual beam system, enabling to monitor ion beam processing with simultaneous Scanning Electron Microscope (SEM) imaging. The FIB column is equipped with a Ga\(^+\) source and was operated at 30 keV, 1 nA beam current. To remove the organic layer it has been used low-dose irradiation \((1.3 \times 10^{16} \text{ ions/cm}^2)\), in order not to mill the substrate. Then, I rinsed the sample with methanol and I grafted PBA nanoparticles from liquid phase [step (3)]. The approach is straightforward because FIB allows high-resolution direct lithography in a single step.

Fig. 7.3(a) shows the result of the FIB patterning that provides irradiated
stripes of 2 µm-width (dark region) alternated with non-irradiated stripes of 5 µm width (light grey). The AFM images in Fig. 7.3(b) show a 3 nm deep groove, whose profile (Fig. 7.3(c)) marks the contours between the irradiated and non-irradiated areas, thus confirming the removal of the organic ligand in the irradiated regions. The smoothness of the edge along the stripes can be estimated better than 10 nm. To demonstrate that any other arbitrary shape can be easily obtained, other lithographic patterns have been manufactured (Fig. 7.4). Panel (a) shows a series of stripes with 100 nm width that were fabricated by selectively removing the organic layer in the black regions. In panel (b), the inverse task was performed, irradiating the whole region except the circles having 2 µm diameter.

After step (3), e.g. the grafting of nanoparticles, SEM and AFM images prove that the nanoparticles only graft on the non-irradiated stripes. The SEM micrograph of Fig. 7.5(a) refers to an area in between an irradiated and a non-irradiated stripe. The different topographic contrast clearly shows that the nanoparticles graft on the non-irradiated region only. The AFM images in Figs. 7.6 confirm this conclusion. A high resolution (10^6 magnification) SEM micrograph (Fig. 7.5(b)), taken at a tilt angle of 52° in order to maximize the surface topographic contrast, shows a density of \( \sim 8 \cdot 10^4 \) particles/µm².

Figure 7.4: SEM image showing a surface patterned with stripes of 100 nm width (a), and circles of 2 µm diameter (b).
Figure 7.5: (a) SEM micrograph demonstrating how particles graft on the non-irradiated areas solely. (b) High resolution SEM image of PBA nanoparticles deposited on unpatterned area. (c) Gaussian distribution of the size of the particles.
Figure 7.6: AFM images taken on the (a) irradiated and (b) non-irradiated region.

The mean height of an individual nanoparticle measured by AFM is \( l_1 \approx 6\, \text{nm} \) (Figs. 7.6). I determined the other two dimensions by SEM (Fig. 7.5(b)). In this way, the size of more than 200 particles map onto a Gaussian distribution (Fig. 7.5(c)) with mean value \( \bar{l} = (8.0 \pm 2.0)\, \text{nm} \) and standard deviation \( \delta = 4.6\, \text{nm} \). The volume of a particle is thus \( v \approx 380\, \text{nm}^3 \). Because of the prolate shape of the nanoparticles, assuming they graft with the largest face, we may estimate the basal dimensions to be \( l_2 = (10.6 \pm 2.0)\, \text{nm} \) and \( l_3 = (6.0 \pm 2.0)\, \text{nm} \).

### 7.2.2 SHPM magnetic imaging

In spite of the efforts in positioning molecular nanomagnets on surface, the magnetic characterization of the resulting coatings - albeit crucial - is still lacking both for technical difficulties (low temperatures and magnetic fields are indeed required) and for the relatively small magnetization of the nano-objects. Here I employ SHPM to describe the magnetic features of molecule-based single-layers for varying temperatures and applied magnetic fields.

The SHPM is inserted in the QD-PPMS cryo-magnetic system working down to \( T = 2\, \text{K} \) and in magnetic field up \( H = 70\, \text{kOe} \). The sample was mounted as sketched in Fig. 7.7(a) on the cryogenic insert. Highly doped Si substrate was used in order to maintain the tunneling operative down to the lowest temperature.

A first set of images of the grafted PBA nanoparticles was obtained at \( T = \)
7. Prussian blue analogs nanoparticles at surface

Figure 7.7: (a) Experimental set-up of the SHPM illustrating the disposal of sample, scanning head and magnetic fields. (b) STM image showing the patterning of the surface. (c) Magnetic image taken simultaneously with (b) and with an applied-field $H = +70$ kOe. The color scale indicates the strength of the detected stray field. The zero-field value of the scale is set to an arbitrary baseline. (d) Same as (c) but with reversed field ($H = -70$ kOe): notice that the color scale is reversed while the same spots are observed.
100 K, e.g. above the ferromagnetic ordering temperature \( T_C \simeq 70 \) K of (NiCr)-PBA. The oblique stripes detected by STM imaging (Fig. 7.7(b)) represent a portion of the patterned texture. Simultaneously, I collected magnetic images by SHPM. At fields as high as \( H = +70 \) kOe, the magnetic profile depicted in panel (c) of Fig. 7.7 shows oblique stripes having the same orientation and pitch as in the STM image. Note that a color scale is utilized to show the intensity of the stray field component \( B_{sf}^z \) perpendicular to the Hall probe. Upon switching the applied field to opposite \( H = -70 \) kOe value, I observed the reversal of the magnetic profile Fig. 7.7(d). This confirms the true (para-)magnetic origin of the stripes, whose colors get more intense along the direction of the applied field. The SHPM images taken on the substrate before the deposition of (NiCr)-PBA nanoparticles, evidence that the metal (Ni-)organic layer does provide no relevant contribution to the signal of Fig. 7.7(c,d).

At temperatures much lower than \( T_C \), each particle develops its own magnetic moment and can thus be treated within the frame of superparamagnetism. Considering the mean size of the ferromagnetic particles, I estimate their magnetic moment to be as large as \( \sim 2 \times 10^3 \mu_B \). Fig. 7.8(a) shows the hysteresis loop of PBA particles when measured by conventional magnetometry on a massive powder specimen. Upon grafting the particles, I collect for \( T = 20 \) K \ll T_C \) a representative series of pictures in Fig. 7.8 on a scan area of \( 7 \times 7 \) µm\(^2\), with the tip in the lift mode (i.e. with no feedback and at fixed height \( h = 350 \) nm from the surface) \(^1\). Specifically, a hysteresis-type cycle is performed by varying the applied field within \( H = \pm10 \) kOe. I note that, for the same conditions of height and \( H \), the color scales in a range of fields that is much stronger than that for \( T = 100 \) K, because of the ferromagnetic transition. In addition, contours are smooth because of the height of the Hall probe from the sample, although the main features are still evident. Oblique stripes are neatly visible for \( H > +1 \) kOe (Fig. 7.8(b-d)). As \( H \) vanishes (Fig. 7.8(e-g)) down to \( H = 0 \) (Fig. 7.8(h)), magnetic spots appear suggesting the presence of random magnetic domains. At

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\(^1\)I chose the working temperature of \( T = 20 \) K because (i) it is well below \( T_C \) and (ii) the width of the scan area \( (7 \times 7 \) µm\(^2\)) is sufficiently large to look at the patterning. At much lower temperatures, i.e. \( 2 \) K, the experimental magnetic images cover areas not larger than \( 4.5 \times 4.5 \) µm\(^2\). For instance, Fig. 7.10 is an image of an area existing within a single stripe for \( T = 2 \) K.
7. Prussian blue analogs nanoparticles at surface

Figure 7.8: (a) Hysteresis loop on a powder sample of (NiCr)-PBA nanoparticles. (b-n) Applied-field evolution of the magnetic domains of the particles grafted on patterned substrate. These images are collected at $T = 20$ K with the tip in the lift mode ($h = 350$ nm). The scan area is $7 \times 7 \ \mu m^2$. The increment of the contour lines is 50 G.
negative fields, the spots rearrange themselves (Fig. 7.8(i-k)) to obtain again the stripe-like shape for $H < -1$ kOe (Fig. 7.8(l-n)), but with opposite direction with respect to positive $H$. For $|H| > 1$ kOe the intensity of the stray field increases without a significant modification of the image.

The topographic studies suggest the particles are elongated along the planar surface. A particle shape anisotropy does thus promote a hard axis of magnetization perpendicularly to the surface. As a consequence, the dipolar field arising from interparticle correlations should lie in the plane. We point out that, in view of the very large magnetic moment per particle and the relatively high surface coverage, the dipolar field is significantly large (see Section 7.1). At zero applied-field one would therefore expect the presence of magnetic domains that should be uncorrelated with respect to the patterned texture, as indeed observed in Fig. 7.8 (h). As the applied field is increased, both anisotropy and dipolar field are overcome and the nanoparticles align along the magnetic field direction. In this situation, strong stray fields are detected in the non-irradiated stripes solely.

To get more details on the stray fields across the patterned texture, we shall
Prussian blue analogs nanoparticles at surface

7. Prussian blue analogs nanoparticles at surface
take images in the tunneling range, so the Hall sensor is closer to the surface 
\( h = 250 \text{ nm} \). Panels (a) and (b) in Fig. 7.9 magnify a restricted area, in which 
we draw a line across an individual stripe as guide to the eyes. For both images, 
we employ an applied-field \( H = +10 \text{ kOe} \). The image (a) collected at \( T = 100 \text{ K} \)
neatly shows that larger magnetic intensities are obtained approaching the border 
from both sides. This changes once we cool down to \( T = 20 \text{ K} \), as indeed depicted 
in panel (b). One can notice that the symmetry is now lost and the largest 
signal is achieved on one side only. The experimental magnetic profiles along the 
reference lines are depicted in panels (c) and (d), respectively. The peculiarities 
in their magnetic profiles can be qualitatively explained by simple micromagnetic 
calculations, for which I assume the stripes to be magnetically uniform. This 
approximation is justified by the relatively large density of particles grafted on 
the surface. Calculations were performed using the software Vizimag [156] that 
numerically solves the equations of the magnetic field in two dimensions. Panels 
(e) and (f) show the calculated results of the magnetic profiles sectioned along 
the lines depicted in the experimental images. The color scale indicates the 
intensity of \( B \). For \( T = 100 \text{ K} \), I consider an out-of-plane magnetization \( M_n \) 
of the stripe, which develops along the applied-field direction. As it can be 
seen, it reproduce well the symmetry of the border effect. For \( T = 20 \text{ K} \), an 
additional in-plane component \( M_t \) of the magnetization of the stripe is needed 
that reproduce the experimental results, for which I assume \( |M_n|/|M_t| = 1.9 \).
The result closely resembles the experimental behavior. The origin of the two 
magnetization components at low temperatures should likely be associated with a 
canting of the Ni and Cr sublattices in the ordered phase, whose onset was already 
detected by magnetization measurements on the bulk equivalent material \(^2\).

I also collected magnetic images at temperatures as low as 2 K. For instance,

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\(^2\)For applied-fields not exceeding 70 kOe, powder samples of the bulk equivalent material 
show molar magnetization values that are roughly 12 % smaller than that expected for full 
ferromagnetic coupling of all Ni and Cr ions [49]. This discrepancy can be accounted for by 
a canting angle of \( \approx 60^\circ \) between the two ferromagnetic Ni and Cr sublattices. Likely, this 
is the result of an intense exchange anisotropy acting on the metal ions. Using \( z = 6 \) for the 
number of nearest neighbors and \( J/k_B \simeq 6.5 \text{ K} \) for the Ni-Cr exchange strength [152], a rough 
mean-field calculation tells us that the exchange field acting on the Ni and Cr ions amounts to 
\( H_{ex} = (2zJ/k_B)S/g\mu_B = 390 \) and 530 kOe for Ni and Cr, respectively.
Fig. 7.10 shows a representative image obtained for $H = 10 \text{kOe}$. The “drawback” of collecting images at such low temperatures is the scan area scaling down to $4.5 \times 4.5 \mu\text{m}^2$ at most. This is not convenient to our purposes since it would not allow us to get an image of the full width of an individual stripe. It is worth pointing out, however, that no time-dependent phenomena were observed while collecting SHPM images during magnetic field cycling. This is not surprising since the magnetic relaxation at 2 K occurs in a time scale ($< 1 \text{s}$, Section 7.1) that is faster than the scanning time (not less than 20 s for a quick SHPM image).

### 7.2.3 Conclusions

In conclusion, I have developed a hybrid procedure that combines liquid phase grafting with direct FIB patterning, by which I was able to deposit hexacyanochromate Prussian blue NiCr nanoparticles on selected portions of Si surfaces. The success of our procedure is demonstrated by locally probing the magnetic properties employing SHPM. The dependencies of the magnetic images on the temperature and applied-field suggest that the bulk equivalent material constituting the nanoparticles comprises two canted magnetic sublattices in its ordered phase.
7. Prussian blue analogs nanoparticles at surface
Part III

Conclusions
Chapter 8

Conclusions

My thesis deals with two main activities: the investigation of the magnetic properties of molecular antiferromagnetic clusters and the development of the scanning Hall microscopy for the study of molecular magnets at surface.

The family of heterometallic antiferromagnetic rings $\text{Cr}_7 M_1 M_2^+ = \text{Cr}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Cu}^{2+}, \text{Ni}^{2+}, \text{Fe}^{2+} \text{and Co}^{2+}$, was synthesized by Dr. G. A. Timco at University of Manchester. The results of the extensive magnetic characterization that I performed allowed to understand the properties of these systems and, in particular, it has demonstrated that the substitution of $\text{Cr}^{3+}$ with divalent metal $M^2+$ allows to tailor their magnetic characteristics (Chapter 3). This systematic work was essential to prepare the focused studies published in Ref. [116–118].

Antiferromagnetic Heisenberg segments can be considered the intermediate step between semi-infinite chains and closed wheels. The synthesis by the molecular approach allows the control of length, doping and spin values. The investigation of these systems allows to get more insight on the nature of the spin excitation, an argument that has found a great relevance in the literature. In collaboration with Dr. S. Carretta, Prof. P. Santini and Prof. G. Amoretti at University of Parma, we discussed the excitations of half-integer spin segments in terms of $L$ and $E$-band, evidencing effects due to the breaking of the cyclic boundary conditions, and the even and odd nuclearity of the system (Chapter 4). In perspective, we plan to investigate new derivatives having integer spin, which
might be relevant for the study the effects of localization of spin excitations [35].

Among the Cr$_7$M wheels, the molecule Cr$_7$Ni has particular relevance for quantum computation. We demonstrated indeed that the ground state of Cr$_7$Ni has total spin $S = 1/2$ and we found that the energy gap between the first excited and ground multiplets is relatively large ($\Delta/k_B \simeq 13$ K), so that low temperature properties can be well described within a two-levels energy pattern (Chapter 5). In collaboration with Dr. F. Troiani (University of Modena and Reggio E.) and group of Prof. G. Amoretti, we also simulated the implementation of one-qubit gate to the molecule of Cr$_7$Ni [118]. Other relevant publications that followed our work (Ref. [135, 136]), have demonstrated that the decoherence time of the molecule of Cr$_7$Ni is relatively long ($3 \mu$s), being approximately $10^4$ times longer that the estimated gating time. This information suggests that Cr$_7$Ni can be successfully considered for processing quantum information.

Afterwards, we explored the possibility to realize dimers of Cr$_7$Ni in which the entanglement of the molecular states is realized with a suitable exchange path. Several derivatives were synthesized following a supra-molecular approach: two molecules of Cr$_7$Ni (alternatively one Cr$_7$Ni and one Co-phthalocyanine) have been linked by amines with H bond inside the ring cavity. The switchability of the interaction was also investigated by inserting a magnetic dimer onto the linking path. We used the dimer of Ru$^{2+}$Ru$^{3+}$ which has two accessible magnetic states via redox reaction. For these systems, the results of the magnetic measurements evidenced that the modifications of the cluster does not alter the original characteristics of Cr$_7$Ni. On the other hand, the interaction was found too weak to give significant effects for $T \geq 0.3$ K. We ascribed this mainly to the small overlap of the molecular orbitals of amine and Cr$_7$Ni core in correspondence to the H-bonds.

A novel family of linked Cr$_7$Ni was recently synthesized in which the amine is directly bonded to a carboxylate bridge. Earliest measurements have been reported in Chapter 5, further work is however needed to understand if the linking path establishes sizable exchange coupling.

The work on selective grafting of Prussian blue nanoparticles at surface was
carried out in collaboration with Prof. T. Mallah and his collaborators at University of Paris Sud - Orsay and Dr. G. C. Gazzadi at CNR - INFM - S3. We developed a new method that combines both the bottom-up (chemical grafting) and top-down (FIB-direct lithography) approach to fabricate patterned single-layers of molecular magnets (Chapter 7). This technique has been successfully implemented for the selective grafting of NiCr-PBA nanoparticles on the surface of SiO$_x$, but in principle it can be used also for other molecular compounds. I used the SHPM to investigate the magnetic properties of these materials. The images I obtained show that the magnetization cycle of the single-layer is comparable to that of the bulk derivative. The effect of canted Ni and Cr sublattices, which has been already observed in the bulk NiCr-PBA derivative [49], was found to be more relevant for the single-layer case.

In the near future, we plan to investigate with SHPM other molecular systems, such as single molecules magnets at surface or extended 2-D self-assembled phthalocyanines.

For the SHPM measurements reported in this work I utilized commercial Hall sensors. Hall probes having very high spatial resolution (down to 50 nm) have been recently realized [74, 75], and this paves the way for the measurements of magnetic field at nanoscale. Our plan is to develop such sensors also for the SHPM in order to improve the spatial resolution of the microscope.
Bibliography


[114] Courtesy of F. Albertini, CNR-IMEM, Parma, Italy.


Curriculum vitae

Alberto GHIRRI
Born in Scandiano (RE), July 7, 1980
Address: via B. Manzini 4, 42019 Scandiano (RE)
Office: +39 0592055678
Mobile: +39 3295810567
E-mail: alberto.ghirri@unimore.it
Internet: http://www.s3.infm.it/

Professional experiences

- 2005 - today
Ph.D. fellowship at CNR-INFM National Research Centre S3 (Modena) and Dipartimento di Fisica, Università di Modena e Reggio Emilia.
Research subject: Studies of molecular antiferromagnetic spin clusters and development of magnetic imaging of surfaces.
My research activity dealt with both the study of the magnetic properties of bulk molecular magnets, and the fabrication and characterization of patterned films of molecular magnets. The experiments on bulk samples were performed by means of calorimetry, ac-dc and torque magnetometry. The magnetic imaging of surfaces was carried out by means of scanning Hall probe microscopy.
Supervisor: prof. Marco Affronte (marco.affronte@unimore.it)
Other contact: dr. Marco Evangelisti (marco.evangelisti@unimore.it)
• **July-December 2004**
  Collaboration with INFM and Dipartimento di Fisica, Universitá di Modena e Reggio Emilia.
  Research subject: Experimental study of molecular magnets.
  Supervisor: prof. Marco Affronte.

• **May and October 2004**
  Specific heat and torque experiments at Grenoble High Magnetic Field Laboratory (GHMFL), CNRS-Grenoble, France.

**Education**

• **2005 - today**
  Ph.D. student, XX ciclo, CNR-INFM National Research Centre S3 (Modena) and Dipartimento di Fisica, Universitá di Modena e Reggio Emilia.
  Thesis title: *Studies of molecular antiferromagnetic spin clusters and development of magnetic imaging of surfaces.*
  Tutor: prof. Marco Affronte.

• **June 2004**
  Laurea degree in Physics at Universitá degli Studi di Modena e Reggio Emilia.
  Thesis title: *Proprietá termodinamiche di anelli antiferromagnetici molecolari.*
  Mark: 110/110 cum laude
  Tutor: prof. Marco Affronte.

• **July 1999**
  High School degree Diploma Perito Industriale at Istituto Tecnico Industriale Statale A. Volta, Sassuolo.
  Mark: 60/60
Other activities

- Contributions to conferences and workshops
  
  
  

- Teaching
  
  Assistant of prof. C. Calandra Buonaura, course of Mechanics for physics and mathematics students at University of Modena and Reggio Emilia (2005-06).
List of publications


• Molecular routes for spin cluster qubits, M. Affronte, F. Troiani, A. Ghirri, S. Carretta, P. Santini, V. Corradini, C. Muryn, G. Timco and R. E. Winpenny, Dalton Transactions 23 (2006), 2810.


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