

Curriculum Vitae

MANUEL MARIANI

Personal Profile

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Education and Positions

- **September 1998**
High School Degree
Scientific Liceo "T. Taramelli", Pavia.
Marks: 56/60

- **June 2004**
 Master Degree in Physics (Solid State Physics)
 University of Pavia – Department of Physics “A. Volta”
 Thesis: “Study of the Phase Separation in Na_xCoO_2 through Nuclear Magnetic Resonance” (Tutor: Prof. Pietro Carretta)
 Marks: 105/110
- **January 2008**
 Doctorate in Physics (Solid State Physics)
 University of Pavia – Department of Physics “A. Volta”
 Thesis: “Spin Dynamics in One-Dimensional and Quasi One-Dimensional Molecular Magnets” (Tutor: Prof. Ferdinando Borsa)
- **November 2007**
 Post Doctoral Fellowship
 University of Pavia – Department of Physics “A. Volta”
 Project: “Characterization of novel magnetic biosensors applied to environment and health science”
- **November 2008**
 Post Doctoral Fellowship
 University of Pavia – Department of Physics “A. Volta”
 Project: “Magnetism”
- **November 2009**
 Post Doctoral Fellowship
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 Project: “Magnetism”
- **November 2010**
 Post Doctoral Fellowship
 University of Pavia – Department of Physics “A. Volta”
 Project: “Magnetic properties of molecular nanomagnets”

Research Activity

Strongly Correlated Electron Systems

The study on this kind of systems focussed on Na_xCoO_2 sample, whose peculiarity is to present properties similar to the ones of the cuprates compounds, precursors of the high T_c superconductors. I studied, through NMR and DC susceptibility measurements, the static and dynamic properties varying the concentration of Sodium inside the sample. NMR

measurements on ^{23}Na e ^{59}Co nuclei, allowed us to evaluate the hyperfine couplings characteristics of these nuclei and to point out, starting from the spectroscopic measurements, the unhomogeneities at a mesoscopic level as detected in from the two components of the absorption spectra of ^{23}Na nucleus to which, depending on the region where the nuclei irradiated are placed, are related different relaxation times of the nuclear magnetization. From the analysis of the static uniform susceptibility and of the spin-lattice relaxation times, the behaviour of the susceptibility proper of the strong correlation systems closet to a quantum critical point, where electronic localization takes place. Summing up we detected the presence of a phase separation inside the system itself, below a critical temperature, between strongly correlated metallic regions and regions characterized by magnetic order. (ref.: P. Carretta et al., *Phys. Rev. B* 70, 024409 (2004))

Low-Dimensional Systems

1D and Quasi-1D Molecular Magnets

The investigation on **$\text{Co}(\text{hfac})_2\text{NITPhOMe}$ (**CoPhOMe**)** “single chain magnet” consisting in 1D chains with Ising-type anisotropy which present a slowing down of the magnetization, through a thermally activated mechanism on decreasing the temperature ($T < 50\text{K}$), focused, with NMR and DC Susceptibility measurements, on the finite-size effects related to the doping of the pure sample with various concentration of Zn^{2+} diamagnetic ions, which break the chains in finite length segments. From NMR measurements we noted that for $T < 50\text{K}$ the inverse of the spin-lattice relaxation time ($T_1^{-1}(T)$) presents two anomalies: un maximum at higher temperature ($T > 15\text{K}$) probably due to the *slowing down* of the magnetization and a large shoulder at low temperature ($T < 15\text{K}$) related to the collective *reversal* of the spins of each segment of the sample which still takes place through an Arrhenius-like mechanism. These peculiar characteristics are coherent with what was observed in AC susceptibility complementary measurements, done by the colleagues of the University of Firenze: for the first time, the hypothesis of the Kinetic Ising Model by Glauber predicted in the 60's, was experimentally verified. It says that in a 1/2-1/2 ferrimagnetic showing an Ising-type anisotropy and with feeble interchain interactions presenta an extreme slowing down of the magnetization and spin freezing before the 3D order can take place, with subsequent long range order happening theoretically at the absolute zero. (refs.: **M. Mariani** et al., *Inorganica Chimica Acta* 360, 3903-3908 (2007); **M. Mariani** et al., *Inorganica Chimica Acta* 361, 4107-4112 (2008))

The family of quasi-1D chains **$\text{Gd}(\text{hfac})_3\text{NITR}$** ($\text{R} = \text{Me}, \text{Ph}, \text{iPr}, \text{Et}$) presents magnetic frustrations because of the competitions between n.n. and n.n.n. exchange intrachain interactions and exchange and dipolar interchain interactions: in the case of $\text{R} = \text{Me}, \text{Ph}$

(weakly-frustrated systems), these compounds present a phase transition from the paramagnetic state to a helical long range 3D ordering (hence these samples are referred as helimagnets); in the case of R=iPr, Et (fully-frustrated systems), these chains fulfill the so-called Villain's conjecture, which consists in a phase diagram characterized by a further chiral phase at intermediate temperature between the paramagnetic and the helical ones. From DC susceptibility, μ SR (muon relaxation rate) and NMR (longitudinal relaxation time (T_1) of the nuclear magnetization of the ^1H nuclei, absorption spectra analysis as a function of temperature) measurements on Gd-Ph, Gd-iPr, Gd-Et derivatives, the expected magnetic properties were verified. In particular in Gd-Ph the helical 3D phase transition was detected from the abrupt increase of the muon relaxation rate del muone in correspondence of the transition temperature; as regards the fully frustrated systems, the 3D phase transitino was noticed on Gd-Et sample and signaled by the sudden increase both of the DC magnetic and susceptibility as a function of temperature and, also in this case, the muon relaxation rate and by a sharp peak in the proton longitudinal relaxation rate associated also to a one order of magnitude broadening of the Full Width at Half Maximum of the ^1H NMR absorption spectra. The specific heat measurements done b the colleagues allowed us to verify completely, for the first time from an experimental point of view, the Villain's conjecture in fully frustrated helimagnets theorized in the 70's. (refs.: **M. Mariani**, *Scientifica Acta* 1, 101-106 (2007); F. Cinti et al., *J. Magn. Magn. Mat.* 310 1460 (2007); **M. Mariani** et al., *Inorganica Chimica Acta* 360, 3903-3908 (2007); F. Cinti et al., *Phys. Rev. Lett.* 100, 057203 (2008); F. Cinti et al., *J. Magn. Magn. Mat.* 322 1259 (2010))

A reasearch activity still in progress regards the (**[Dy(hfac)₃{NIT(Et)}]**) single chain magnet and the **Dy(hfac)₃{NIT(C₆H₄OPh)}** quasi-1D systems which are chemically "built" with the same chemical building blocks (regular pattern of Dy ions and radical centres along the chains) but they have different features depending on the radical inserted in the compound: in fact while the latter sample possesses a long range 3D order at $T \sim 4.2\text{K}$, the former behaves like CoPhOMe mentioned above and thus obeys the *Kinetic Ising Model* by Glauber. Also on these systems the characterization measurements of the static and the dynamic properties of the spin include the spin-spin (T_2) and spin-lattice T_1 nuclear relaxation times of ^1H nuclei and their absorption spectra, the muon relaxation rate and the DC susceptibility as a function of temperature and of the static magnetic field applied.

Molecular Clusters

A molecular cluster which showed peculiar magnetic properties is **Ni₁₀**. The magnetic core of the sample is constituted by ten Ni^{2+} ions arranged in a supertetrahedron; the different magnetic centres which belongs to the system are separated enough among them so that each one can be studied separately. The NMR measurements of the absorption spectra of the ^1H nuclei and of their spin-lattice relaxation rate as a function of temperature and of the static

magnetic field applied were of fundamental importance for these sample. Through these experiments we pointed out a form of non-equilibrium bulk magnetization at temperatures of about 17K: the NMR measurements demonstrated that the blocking of the macroscopic magnetization is not related to the freezing of the magnetic moments of the Ni atoms, in contrast with the behaviour of the blocked superparamagnetic systems, the single-molecule magnets and the spin glass. Hence we supposed that the *slowing down* of the magnetization is related to a resonant phonon trapping mechanism which prevents the thermalization of the magnetization but allows the fast spin flipping of each magnetic moment of the molecule. (ref.: M. Belesi et al., *Phys. Rev. Lett.* 102, 177201 (2009))

The two clusters **Cu₆Fe** e **Cu₆Co** studied simultaneously with the NMR technique on ¹H and the DC magnetic susceptibility. Cu₆Fe is constituted by a six Cu²⁺ and one Fe³⁺ ions core (both the ions have s=1/2) presents a weak ferromagnetic exchange interaction with J=0.14K between the Cu²⁺ ions through the iron ion, while Cu₆Co, where the Co³⁺ ion is diamagnetic, is characterized by a weak antiferromagnetic exchange interaction with J=-1.12K as experimentally verified through susceptibility measurements performed as a function of temperature. The nature of the interactions was detected also from the T₁ relaxation time which is temperature independent, characteristic of the paramagnetic systems and that below T=2K follows the same behavior of the susceptibility with an upturn for the first system and a downturn for the second compound. These two samples, which remain in a paramagnetic phase till very low temperature, can be classified in a new family of compounds which can be called single-molecule paramagnets. This property can be attributed to the fact that the intramolecular interaction results to be weak to be compared to the intermolecular one inside the crystal where there are the molecules, differently from the previous rings where the intermolecular interactions were negligible and each molecule behaves as a isolated system. (ref: P. Khuntia et al., *Phys. Rev. B* 80, 094413 (2009))

A heterometallic metallic ring of the family of the clusters derived from the homometallic Cr₈, is **Cr₇Fe**. I studied this system by means of proton NMR as a function of temperature and of the field applied and through DC magnetic susceptibility. The synthesis of this sample was made by substituting of one of the Cr³⁺ (s=3/2) ions, with a Fe²⁺ (s=2) ion. The system is characterized by antiferromagnetic exchange interactions both among Chromium ions and between Chromiums and Iron ion, giving rise to a ground state whose total spin is S_T=1/2. From the susceptibility data written as 1/χ vs T we were able to calculate the intensity of the antiferromagnetic coupling between Cr³⁺ ions which resulted to be J_{Cr-Cr}=13±1K. The measurements of the spin-spin relaxation time showed a great signal loss of the NMR signal of the protons, because of the wipe-out effect, already observed in other molecular nanomagnets with a magnetic ground state, which consists, for a high percentage of the irradiated nuclei, in a relaxation faster than the dead time of the electronics of the instrumentation use, with the subsequent loss of part of the information regarding the spin dynamics. From the analysis of

the absorption spectra and of the T_1 we can deduce that the inhomogeneous linewidth and the spin-lattice relaxation rate are driven and dominated by the dipolar interaction between the nuclei and the magnetic moments of the paramagnetic ions of the cluster. All the phenomena discovered in this compound can be qualitatively justified with the use of a single correlation frequency depending on the temperature which characterizes the spin dynamics of the antiferromagnetic rings and from the data analysis, it results to be, in this sample, of one order of magnitude greater with respect to the one of the homometallic compound. (ref: H. Amiri et al., *Phys. Rev. B* 81, 104408 (2010))

A new project I'm involved in regards a new class of clusters. These systems can be thought as an evolution of the classical ones, since, differently from the previous rings, where each molecule in the crystal, thanks to the chemical ligands, was isolated from the adjacent analog molecule, the chemists try to couple the molecule through the so-called coordination chemistry, that is to say inserting magnetic links between the two units, in order to create exchange and superexchange interactions. The compound under the study for the magnetic characterization through NMR technique (absorption spectra and relaxation times of ^1H nuclei as a function of temperature and magnetic field) is the system of Cr_7Ni rings connected two by two by a single magnetic centre consisting of Cu^{2+} ion. Susceptibility measurements seem to suggest an exchange interaction with $J=1\text{K}$ between the Copper link and each of the two clusters. The aim of the investigation is to compare the spin dynamics between the system of the isolated rings and the system of so-called entangled clusters, which could have promising applications in nanotechnology as qubits.

Magnetic Biosensors

The research activity I'm involved in and which is related to applications to the everyday life is the one related to prototype biosensors of high sensitivity and based on magnetic field detection. These are synthesized at ISPRa centre laboratories and measured by me in order to test their efficiencies for possible future applications in biomedicine. The main issues to be faced were: 1) the best technique for immobilization of molecular probes on the surfaces 2) the most promising magnetic nanoparticles to target the biomolecule 3) the study of the sensitivity of the biosensors detection mechanism by means of SQUID magnetometry. The minimum requirements for a further development of these prototypes is to obtain a coherent reproducible SQUID detection of the magnetic moment. The preliminary measurements on magnetic moment at room temperature in different stages of the preparation were encouraging, showing an increase of the magnetic moment after the adsorption of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) superparamagnetic nanoparticles and a subsequent reduction after the adsorption of IgG (human Immunoglobulin G) whose contribution is diamagnetic. In order to improve the reproducibility of the detection and to optimize the specific detection of the biosensor, we

compared the adsorption of a standard protein such as albumin and the adsorption of PBS (Phosphate Buffered Saline). Even though we tested three different protocols for this purpose, the SQUID measurements results didn't permit any specific detection, indicating also a low degree of reproducibility of the measurement. The objective is now headed to a better control of growth methods and parameter to synthesize prototype sample to obtain improved performances.

Magnetic Nanoparticles as MRI Contrast Agents

A big project involving various Universities research centres, I took part, regarded the development of novel contrast agents for MRI. The tested contrast agents are constituted by para- and superparamagnetic nanoparticles: the former are Gadolinium-based, the latter are made up of Ferrites and Manganese and Cobalt Ferrites dispersed both in apolar solvent and in water in order of a real comparison with the commercial contrast agents such as Endorem and Sinerem also water dispersed. All the particles were coated by oleic acid or an amphiphilic polymer suitable for water transfer. In this project, where all the participants took care of all the stages starting from the synthesis of the samples, passing through the topological and magnetic characterization, to the MRI tests, I measured the transverse (r_2) and longitudinal (r_1) relaxivity as a function of frequency of the prototype contrast agents: in practice I measured the NMR dispersion curves of the samples. The investigation of the performance of these contrast agents focused mainly on the dimensions of the inorganic core of the nanoparticles and on the coating, the last one tested in order to be biocompatible for medical applications. We especially noticed that the contrast agents containing nanoparticles based on Manganese and Cobalt ferrites show relaxivities comparable or even greater than the commercial samples, in particular in the frequency range of clinical interest. This result is very important since, once passed the toxicity tests, these contrast agents can be patented and become commercial with the achievement of better performances than the ones available at the moment. This research is still open to optimize these compounds as regards the chemical synthesis to have the complete control on their dimensions, shape, in order to be reproducible, both for a systematic study of the mechanisms responsible for the nuclear relaxation and for their clinical use in the MRI technique. (ref.: A. Boni et al., *J. Phys. D: Appl. Phys.* 41, 134021 (2008))

The collaborations in these research projects involved and still are involving DISMAB of the University of Milano with the group of Prof. A. Lascialfari which there is a continuous collaboration with, for the NMR measurements in all the projects, the group of Prof. D. Gatteschi of the Department of Chemistry of the University of Firenze for the experimental studies on the low-dimensional systems among them the one related to the magnetic

nanoparticles (in this research there is also a collaboration with the Department of Chemical Science of the University of Cagliari (Prof. M.F. Casula group) and with Bracco S.p.A., Bruker Biospin s.r.l. e Colorobbia Cericol industries) and the Department of Physics with Prof. A. Rettori and Prof. M.G. Pini for the theoretical interpretations regarding 0D and 1D systems. A fruitful collaboration is intense also with the Departments of Physics of the University of Fisica (Prof. M. Affronte group) and of the University of Parma (Prof. P. Santini group) for the experimental and theoretical investigations of the clusters, the Department of Chemistry of the University of Bucharest (Prof. M. Andruh group) and the Lewis Laboratory of Magnetism of the University of Manchester (Prof. R.E.P. Winpenny group) for the classical and entangled rings.

Experimental Techniques

- NMR of solids (single crystals and powders) and liquids
- Basics of MRI and practice in the use of tomography
- μ SR of solids (single crystals and powders)
- SQUID measurements (M_{vsH} , M_{vsT}) of solids (single crystals and powders)

Conferences

1. ***ECMM 2006 (10-15 Ottobre 2006, Tomar (Portogallo) : poster*** titled “NMR Investigation on Spin Dynamics in Pure and Zinc-Doped $\text{Co}(\text{hfac})_2\text{NITPhOMe}$ Single-Chain Magnet”
2. ***SCES 2007 (13-18 Maggio 2007, Houston (Texas, USA)) : poster*** titled “Investigation of spin dynamics in one-dimensional molecular magnets”
3. ***E-MRS 2007 Spring Meeting (28 Maggio–1Giugno 2007, Strasburgo (Francia)) : poster*** titled “Investigation of spin dynamics in one-dimensional molecular magnets”
4. ***Convegno Internazionale “Nanotec2008.it-Nanotecnologie per l’Industria 2015” (10-13 Marzo 2008, Venezia (Italia))***
5. ***ANM 2008 Spring Meeting (22-25 Giugno 2008, Aveiro (Portogallo)) : poster*** titled “NMR investigation of spin dynamics in rare-earth-based molecular chains”

6. **ICMM 2008 (21-24 Settembre 2008, Firenze (Italia))** : posters titled “ μ SR investigation of spin dynamics in pure and Zn-doped $\text{Co}(\text{hfac})_2\text{NITPhOMe}$ single-chain magnet” and “Nuclear Magnetic Resonance studies of novel Mn-ferrites and Co-ferrites based MRI contrast agents”
7. **Transalp’Nano 2008 (27-29 Ottobre 2008, Lione (Francia))** : poster titled “Nuclear Magnetic Resonance investigation of Mn-ferrites and Co-ferrites based MRI contrast agents”
8. **NNC (National Nanomedicine Conference) 2008 (28-29 Novembre 2008, Genova Italia)** : oral contribution titled “Nuclear Magnetic Resonance Investigation of Novel Mn-Ferrites and Co-Ferrites based MRI Contrast Agents”
9. **6th Conference on FFC NMR Relaxometry (4-6 Giugno 2009, Torino (Italia))** : oral contribution titled “Nuclear Magnetic Resonance Investigation of Novel Mn-Ferrites and Co-Ferrites based MRI Contrast Agents”
10. **ICM 2009 (26-31 Luglio 2009, Karlsruhe (Germania))** : poster titled “NMR Study of the Magnetic Properties in one-dimensional Dysprosium-based Molecular Magnets”
11. **ECMM 2009 (4-7 Ottobre 2009, Wroclaw (Polonia))** : poster titled “NMR Investigation of $\text{Gd}(\text{hfac})_3\text{NITet}$ Fully Frustrated XY Helimagnet”
12. **MAGNET '09 – I Convegno Nazionale di Magnetismo (27-29 Ottobre 2009, Roma (Italia))** : poster titled “NMR Study of the Spin Dynamics of $\text{Gd}(\text{hfac})_3\text{NITet}$ Fully Frustrated XY Helimagnetic Chains”
13. **RISONANZA MAGNETICA IN MEDICINA: dalla ricerca tecnologica avanzata alla pratica clinica (4-5 Febbraio 2010, Milano (Italia))** : poster titled “NMR Study of Novel Contrast Agents for MRI based on Mn-Ferrites and Co-Ferrites”
14. **3°FORUM Nazionale dei Giovani Ricercatori di Scienza e Tecnologia dei Materiali (22-24 Marzo 2010, Padova (Italia))** : poster titled “Magnetic Properties and Spin Dynamics in Heptanuclear Single-Molecule Magnets: $\text{Cu}_6\text{Fe Cu}_6\text{Co}$ ”

15. **Joint Euromar 2010 and 17th ISMAR Conference (4-9 Luglio 2010, Firenze (Italia))** : poster titled "Validation of the Villain's Conjecture in Gd(hfac)₃NITe Fully Frustrated XY Helimagnet: a NMR Study"

Schools

1. **XI Scuola Nazionale in Scienza dei Materiali** (17-22 Ottobre 2005, Cortona (AR) (Italia))
2. **Training School on NMR, NQR, μ SR and Mossbauer Techniques** (17-30 Settembre 2006, Pavia (Italia))

Publications

1. P. Carretta, **M. Mariani**, C. B. Azzoni, M. C. Mozzati, I. Bradaric, I. Savic, A. Feher, J. Sebek, *Phys. Rev. B* 70, 024409 (2004)
2. **M. Mariani**, *Scientifica Acta* 1, 101-106 (2007)
3. F. Cinti, A. Rettori, M. Barucci, E. Olivieri, L. Risegari, G. Ventura, A. Caneschi, D. Gatteschi, D. Rovai, M. G. Pini, M. Affronte, **M. Mariani**, A. Lascialfari, *J. Magn. Magn. Mat.* 310 1460 (2007)
4. **M. Mariani**, S. Aldrovandi, M. Corti, J. Lago, A. Lascialfari, E. Micotti, A. Rettori, F. Cinti, A. Amato, C. Baines, L. Bogani, A. Caneschi, S.P. Cottrell, D. Gatteschi, *Inorganica Chimica Acta* 360, 3903-3908 (2007)
5. F. Cinti, A. Rettori, M. G. Pini, **M. Mariani**, E. Micotti, A. Lascialfari, N. Papinutto, A. Amato, A. Caneschi, D. Gatteschi, M. Affronte, *Phys. Rev. Lett.* 100, 057203 (2008)
6. **M. Mariani**, S. Aldrovandi, M. Corti, A. Lascialfari, L. Bogani, A. Caneschi, R. Sessoli, *Inorganica Chimica Acta* 361, 4107-4112 (2008)

7. A. Boni, M. Marinone, C. Innocenti, C. Sangregorio, M. Corti, A. Lascialfari, **M. Mariani**, F. Orsini, G. Poletti, M. F. Casula, *J. Phys. D: Appl. Phys.* 41, 134021 (2008)
8. M. Belesi, E. Micotti, **M. Mariani**, F. Borsa, A. Lascialfari, S. Carretta, P. Santini, G. Amoretti, E. J. L. McInnes, I. S. Tidmarsh, J. R. Hawkett, *Phys. Rev. Lett.* 102, 177201 (2009)
9. S. Tambalo, A. Daducci, S. Fiorini, F. Boschi, **M. Mariani**, M. Marinone, A. Sbarbati, P. Marzola, *Magnetic Resonance in Medicine* 62, 4, 1080-1084 (2009)
10. P. Khuntia, **M. Mariani**, M. C. Mozzati, L. Sorace, F. Orsini, A. Lascialfari, F. Borsa, M. Andruh, C. Maxim, *Phys. Rev. B* 80, 094413 (2009)
11. H. Amiri, **M. Mariani**, A. Lascialfari, F. Borsa, G. A. Timco, F. Tuna, R. E. P. Winpenny, *Phys. Rev. B* 81, 104408 (2010)
12. F. Cinti, A. Rettori, M.G. Pini, **M. Mariani**, E. Micotti, A. Lascialfari, N. Papinutto, A. Amato, A. Caneschi, D. Gatteschi, M. Affronte, *J. Magn. Magn. Mat.* 322 1259 (2010)

Languages

- English: fluent
- French: fluent

Pavia, February 8th 2011

Manuel Mariani