称号及び氏名　　博士(理学)　 Miguel Pardo Sainz

学位授与の日付　2024 年 9 月 23 日

論　　文　　名　Non-collinear magnetism in chiral, spinel and organic magnets
(キラル、スピネル、有機マグネットにおける非共線磁性)

論文審査委員　　主査　　細越　裕子
副査　　会沢　成彦
副査　　久保田　佳基
副査　　小野　俊雄
副査　　Javier　Campo

Thesis Abstract

Non-collinear magnetism in chiral, spinel and organic magnets

キラル、スピネル、有機マグネットにおける非共線磁性

Miguel Pardo Sainz

ミゲル・パルド・サインス

Magnetism has intrigued humans for centuries, transitioning from early discoveries of lodestones to a core element in modern technology and physics, impacting daily life and global issues such as climate change and energy sustainability. Recently, the field of non-collinear magnetism, featuring unique, tilted magnetic alignments within materials, has emerged, offering new potential for developing intricate and efficient magnetic structures. In this doctoral thesis, conducted in joint supervision between the University of Zaragoza and the Osaka Prefecture University, we consider three factors that can contribute to non-collinear magnetism: the antisymmetric Dzyaloshinskii-Moriya (DM) interaction, magnetic frustration in Heisenberg exchange interactions, and magnetic anisotropy due to the crystal field effect. These factors, influenced by crystal symmetry and geometry, can lead to topologically non-trivial magnetic textures with a variety of length scales and physical properties. Specifically, this thesis focuses on the sources of non-collinear magnetism in three key types of materials: chiral, spinel, and organic magnets, each presenting unique challenges and opportunities. The study of these materials opens the door not only to theoretical advances but also to revolutionary technological applications, from high-density and energy-efficient information storage solutions to the forefront of quantum computing and the development of next-generation sensors.

The thesis is organized into three parts, each exploring a different source of non-collinear magnetism in multifunctional materials. After a general introduction to experimental techniques, the first part focuses on the role of antisymmetric DM interactions in generating non-collinear magnetic phases in the cubic chiral magnets MnSi and $Fe_{0.75}Co_{0.25}Si$.

- To confirm previous theories about the existence of new magnetic phases in MnSi, specific heat and magnetization curves (d.c. and a.c.) were measured as a function of field and temperature. An anomaly is clearly observed in the a.c. magnetization, suggesting the existence of a new phase that could correspond to the predicted unknown state. To

understand the possible differences between this new phase (*B-phase*) and the skyrmion phase (*A-phase*), experiments were carried out with neutron scattering (SANS) and muon spin rotation (μSR) techniques. The results indicate that the *B-phase* could be compatible with a reorientation of the magnetic helices in MnSi. Additionally, the μSR experiments in the *A-phase* highlight the need for a detailed theoretical study of the skyrmion lattice profile in MnSi.

- The effect of disorder in the compound $Fe_{0.75}Co_{0.25}Si$ was also investigated using d.c. and a.c. magnetization, SANS, and μSR. The results reveal anomalies in the a.c. magnetization similar to those observed in MnSi, as well as a dependence of the stability of the B-phase on the history and direction of the magnetic field, suggesting the influence of chemical disorder in the development of the *B-phase*. The SANS experiments show that such disorder also alters both the structure of the skyrmion lattice (*A-phase*) and its stability. Additionally, they allow discarding the same origin for the *B-phase* as proposed in other materials. The analysis of the μSR data shows a wide distribution of local fields, suggesting a combination of the range of possible muon implantation sites and an increase in magnetic fluctuations induced by substitutional disorder.

The next part explores the combined effect of frustration and disorder on the magnetic properties of the spinel families $Mn_{1-x}Mg_xCr_2O_4$ and $CuCr_{2-x}Sn_xSe_2S_2$.

- The nuclear and magnetic structure of the spinel $MnCr_2O_4$ has been reinvestigated as a function of temperature in powder samples synthesized under different conditions, using magnetization, specific heat, and neutron powder diffraction (NPD) experiments. These experiments confirm the existence of three long-range order (LRO) magnetic phases; a ferrimagnetic (FIM) phase, an incommensurate spiral phase, and a new phase, never reported before. The symmetry of each magnetic phase has been determined using the formalism of magnetic superspace groups (MSSG). The transition temperatures of the three magnetic phases depend on the atmosphere in which the samples were synthesized. A possible explanation for these transitions has been discussed based on experimental and theoretical results. Finally, the presence of transverse conical magnetic structures allows for the existence of multiferroicity, and the direction of electric polarization has been derived using the spin current model.

- Next, the effect of magnetic disorder in the $Mn_{1-x}Mg_xCr_2O_4$ family has been studied. NPD experiments similar to those performed for $MnCr_2O_4$ ($x = 0$) show that the nuclear symmetry is analogous to that of said compound over a wide range of temperatures. For low Mg contents, the same FIM and incommensurate spiral phases, both long-range, are observed. As the Mg content increases, the FIM phase is no longer observed, while the spiral order transitions from long to short range, forming small clusters. The evolution of magnetic order with x agrees with previous studies, explained by the weakening of exchange interactions and the compression of Cr-O octahedra as the Mg content increases.

- A structural and magnetic characterization has been carried out in solid solutions of the $CuCr_{2-x}Sn_xSe_2S_2$ family using d.c. and a.c. magnetization, high-resolution transmission electron microscopy (HRTEM), and NPD experiments. The crystal structure of these spinel series has been refined, revealing a new and unexpected monoclinic secondary phase. The magnetism of these compounds is understood as the result of a random competition between ferromagnetic Cr^{3+} -Cr^{4+} interactions (double exchange process) and antiferromagnetic Cr^{3+}- Cr^{3+} interactions (superexchange process). Our results allow proposing a long-range FM order for samples with $x \leq 0.4$. In samples with a relatively high Sn concentration ($x > 0.4$), frustration and random diamagnetic dilution by Sn suppress the long-range FM order, replacing it with spin glass-like behavior.

In the last part, we examine the evolution of the magnetic properties with dimensionality in the purely organic magnets 4-F-2-NNBIP and $TNN \cdot CH_3CN$, which exhibit a combination of low anisotropy and frustration.

- The organic compound 4-F-2-NNBIP has been characterized using X-ray diffraction, electron paramagnetic resonance (EPR), specific heat, magnetization, and susceptibility measurements at high magnetic fields and very low temperatures. Numerical calculations have also been performed to obtain the relevant magnetic parameters of the system. The joint analysis of diffraction data and EPR measurements implies that this system can be described by a two-leg antiferromagnetic Heisenberg ladder with $S = 1/2$. The magnetic exchange interactions have been estimated from the fit of the susceptibility data using quantum Monte Carlo (QMC) and exact diagonalization (ED) calculations. With the help of specific heat data, we propose a phase diagram with 3 distinct magnetic phases: a quantum disordered (QD) or spin liquid phase, a phase with gapless excitations (Luttinger liquid (LL) or quantum critical paramagnet (QC)), and a fully polarized (SP) phase. In addition, a region is observed where magnetization data deviate from theory, and several models to account for this deviation are proposed.

- Finally, the organic compound $TNN \cdot CH_3CN$ has been studied, focusing on the determination of its magnetic structure at low magnetic fields using single crystal neutron diffraction (SCND), polarized neutron diffraction (PND), and μSR experiments. At zero field, the magnetic signal is too weak to be observed in SCND experiments. Nevertheless, by making use of a computational model and DFT calculations, the absence of oscillations in the μSR spectra is shown to be compatible with high-symmetry magnetic structure at the muon site. The proposed magnetic configuration is consistent with previous studies, as well as with theoretical predictions of its multiferroic nature. The trimer formation is also explored at the 1/3 plateau ($1.25 \leq B \leq 8.49$ T). After a low-temperature magnetic and structural characterization, the spin density distribution has been obtained from PND experiments by using the wavefunction and multipole approach. The computational model used to interpret the μSR spectra agrees with the PND results and the theoretical ground state, where the magnetic moment in the TNN molecule is equally distributed among the three NN radicals.

In conclusion, novel magnetic phases have been identified in chiral magnets, highlighting the critical role of DM antisymmetric interactions and the intricate interplay between disorder, anisotropy and temperature in dictating the stability and characteristics of such phases. The findings on magnetic spinels have revealed how magnetic frustration and disorder intertwine to influence the material's magnetic properties and manifest complex magnetic behaviors. The results on organic magnets have not only bridged theoretical predictions with experimental validation, but also exemplified the sophisticated interplay of structure, magnetism, and topology in low-dimensional organic systems. These findings collectively underscore the multifaceted origins of non-collinear magnetism, propelled by intrinsic and extrinsic factors, and underscore the potential for topologically non-trivial magnetic textures across different material systems.

Publication List

- Small Angle Neutron Scattering Study near the Critical Field at Low Temperature in MnSi, Ohishi, K.; Kousaka, Y.; Iwasaki, S.; Akimitsu, J.; Pardo-Sainz, M.; Laliena, V.; Campo, J.; Ohkuma, M.; Mito, M., JPS Conf. Proc. 33, 011060 (2021) / Already published.
- New Magnetic Intermediate State, “B-phase,” in the Cubic Chiral Magnet MnSi, Ohkuma, M.; Mito, M.; Pardo, M.; Kousaka, Y.; Iwasaki, S.; Ohishi, K.; Akimitsu, J.; Inoue, K.; Laliena, V.; Campo, J., APL Mater., 10, 041104 (2022) / Already published.
- New (α β γ)-Incommensurate Magnetic Phase Discovered in the MnCr2O4 Spinel at Low Temperatures, Pardo-Sainz, M.; Toshima, A.; André, G.; Basbus, J.; Cuello, G.J.; Laliena, V.; Honda, T.; Otomo, T.; Inoue, K.; Hosokoshi, Y.; Kousaka, Y.; Campo, J., Phys. Rev. B., 107, 144401 (2023) / Already published.
- Suppression of Ferromagnetism and Emergence of Spin-Glass Like Behavior in the CuCr2-xSnxS2Se2 Spinels, Pardo-Sainz, M.; Moris, S.; Piquer, C.; Rodríguez-Velamazán, J.A.; López, M.L.; Álvarez-Serrano, I.; Galdámez, A.; Campo, J., Phys. Rev. B. (2024) / Under submission.
- Quantum criticality and anomalous magnetization in a purely organic spin ladder, Pardo-Sainz, M.; Ono, T.; Díaz-Ortega, I. F.; Kihara, T.; Nojiri, H.; Kono, Y.; Sakakibara, T.; Yamaguchi, H.; Laliena, V.; Hosokoshi, Y.; Campo J. / Planned on submitting to Phys. Rev. B within six months.

学位論文審査結果の要旨

申請者氏名：Miguel Pardo Sainz（ミゲル・パルド・サインス）
学位論文題目：Non-collinear magnetism in chiral, spinel and organic magnets
(キラル、スピネル、有機マグネットにおける非共線磁性)

磁性研究において、近年、物質内部の磁気配列が、平行・反平行から傾いた非共線的である場合に現れる、特異な磁気状態に興味が持たれている。このような非共線磁性が現れる要因として、反対称ジャロシンスキー・守谷(DM)相互作用、磁気フラストレーション、磁気異方性が考えられる。本研究は、非共線磁性の起源に着目し、キラル、スピネル、有機磁性体の 3 種類について、磁化、比熱等の巨視的磁気測定に加え、中性子線散乱やミュオンスピン回転(μSR)などの微視的な磁気測定手法を用いて、磁気構造の解明研究を行った。

本論文は、第 1 章で研究背景を概説し、第 2 章で実験方法を述べ、以降、3 パートで構成される。パート I は立方晶系キラル磁性体を扱い、反対称 DM 相互作用によって生じるらせん磁気配列を明らかにした。キラル磁性体 MnSi を第 3 章で扱い、スキルミオン相(A 相)および未知の磁気相(B 相)について、らせん磁気配列の再配列を明らかにした。これと磁気異方性の異なるキラル磁性体 $Fe_{0.75}Co_{0.25}Si$ を第 4 章で扱い、化学的不規則性が、局所磁場の分布や非共線磁気相の安定性に影響することを明らかにした。パート II は磁性スピネル化合物について、磁気フラストレーションと無秩序性を起源とする非共線磁気構造を明らかにした。磁気フラストレーションを示す $MnCr_2O_4$ について第 5 章で扱い、3 つの磁気秩序相－フェリ磁性(FIM)相、不整合スパイラル(IS)相、未知の磁気相を観測し、これらの対称性を磁気超空間群によって決定した。$Mn_{1-x}Mg_xCr_2O_4$ の磁気的乱れの効果を第 6 章で扱い、非磁性 Mg 含有量と FIM 相や IS 相との相関を明らかにした。第 7 章では、$CuCr_{2-x}Sn_xSe_2S_2$ の磁性が、Cr^{3+}-Cr^{4+}の二重交換相互作用による強磁性相互作用と、Cr^{3+}-Cr^{3+}の超交換相互作用による反強磁性相互作用のランダムな競合として理解できること、Sn 濃度によるランダムな非磁性希釈と、磁気フラストレーションによって、強磁性秩序からスピングラス挙動への変化を観測した。パート III では、磁気異方性の小さい有機磁性体について理論的予測の実験的検証を行うともに、低次元性と磁気フラストレーションによって生じる非共線磁性を扱った。2 本足梯子鎖反強磁性体 4-F-2-NNBIP を第 8 章で扱い、3 つの磁気相－量子無秩序相(スピン液体相)、ギャップレス相（朝永-ラッティンジャースピン液体相あるいは量子臨界常磁性相)、磁気飽和相を観測した。飽和磁化近傍に非自明な磁気相が示唆された。分子内に 3 つのラジカル基を含む三角スピン TNN・CH_3CN を第 9 章で扱い、低磁場相における、分子内のスピン分布および結晶中の磁気構造決定を行った。最後に、本論文の結論を述べている。

以上のように、本研究は、非共線磁性の起源と磁気配列を解明し、磁気構造を設計する基礎ともなる重要な研究成果と言える。本委員会は、本論文の審査、最終試験の結果に基づき、博士（理学）の学位を授与することを適当と認める。

委員長　細越　裕子
会沢　成彦
久保田 佳基
小野　俊雄
Javier Campo