Commission on Magnetic Structures

MAGNETIC-STRUCTURE RESEARCH: CURRENT AND FUTURE TRENDS

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Keywords: magnetic structures, symmetry-based computational tools, instrumentation, magnetic structure database

Abstract

We present the status of research of magnetic structures and outline future developments.

Introduction

Magnetic structure refers to the arrangement of magnetic moments in a crystal. Within this context, the determination and application of magnetic structures comprise an important subfield of structural crystallography. A know -ledge of the magnetic order in a material is essential for understanding its physical properties, and is relevant to both basics and applied materials research in many disciplines of science and technology, including physics, chemistry, material science, geology, biology, and engineering. The IUCr Commission on Magnetic structures represents a broad multidisciplinary community of researchers who develop experimental and computational tools, acquire neutron and x-rays scattering data, determine magnetic arrangements, related magnetic structure to physical properties, and disseminate research outputs. At this moment in time, we observe and anticipate rapid development of this research field in the following directions:

1. Infrastructure for determining and using magnetic symmetry
2. Instrumentation and software for collecting and reducing magnetic scattering data
3. Software for magnetic structure solution
4. Greater scope and improved accessibility of known magnetic-structure data
5. New basic and applied science involving magnetic degrees of freedom

1. Infrastructure for determining and using magnetic symmetry

Magnetic symmetry is an essential tool in detecting, understanding, describing, modeling, predicting, and experimentally determining long and short-range magnetic order. Magnetic point symmetries fundamentally restrict the tensor properties of magnetic materials. Magnetic translational and point-translational symmetries further enable finite models of highly complex magnetic orderings that are both compact and unambiguous. The 122 magnetic point groups (MPGs) in three dimensions were originally derived by Heesch [1] and later reintroduced by Shubnikov and Zamorzaev. The 1651 magnetic space groups (MSGs) were first tabulated by Belov, Neronova, and Smirnova [2] and later by Oppechowski and Guccione [3]. The magnetic superspace groups (MSSGs), which are relevant to incommensurate magnetic structures [4], are currently being tabulated for up to 3+3 dimensions [5].

Representation analysis (RA) is another commonly used approach to describing the order parameters that arise in phase transitions, and was first applied to magnetic structures in 1962 by Alexander [6]. This approach was the default until fairly recently, when modern infrastructure for the use of MSGs became readily available [7-9]. It is now well understood that RA and MSG restrictions are fully compatible, and in fact provide complimentary constraints on magnetic models [4, 10]. In recent years, the combined use of RA and MSGs has become a very useful tool for professionals and gained popularity even among non-specialists with the development of computer programs like Fullprof [11], JANA[12], Mody [13], SARAh [14], and TOPAS Academic [15].

The nowadays rapid progress in this area has been substantially accelerated by the availability of computer-readable magnetic symmetry-group and magnetic group-representation data through the Bilbao Crystallographic Server [7] and the Isotropy Software Suite [8]. These tools are very general in their application of group theoretical methods to the analysis of phase transitions in the crystals.

2. Instrumentation and software for collecting and reducing magnetic scattering data

Magnetic structures are usually solved from neutron diffraction data. This concerns not only long-range orders but also short-range states studied with the help of diffuse scattering. Neutron data are more confined due to lower flux of the neutron sources compared to x-ray synchrotron diffraction data used for solution of crystal structures. Therefore one of the targets of the magnetic diffraction community is the development of neutron sources and instruments allowing fast collection of magnetic intensities from small samples, delivering data comparable in quantity and quality to X-ray synchrotron data. Building and designing of new neutron sources, which nowadays are mainly spallation sources, and increase of the flux of the existing neutron reactors is boosting construction of high-flux, high-resolution powder and single crystal diffractometers. They are equipped with large area detectors and fast time-resolved electronics. New generation of the solid-state detectors is now under development to replace the traditional expensive ^{3}He detectors [16].Polarised neutron diffractometers, which are extremely useful for separation of magnetic scattering from nuclear and incoherent components, profit from the technical developments of neutron polarisers and wide-angle polarisation analysers. This new neutron optics allows also collection of large Q-range data with improved peak-to-background ratio. It is worth mentioning a challenging idea of the construction at the European spallation source ESS of a dedicated single crystal diffractometer MAGIC [17] fed by both, cold and thermal, polarised neutron beams. Realization of this idea could solve the need of the community for fast-acquisition, high-quality, high-resolution magnetic single crystal data.

Similarly important is the development of X-ray synchrotron beamlines for measurement of resonance and non-resonance magnetic scattering. A huge progress is achieved in this technique since pioneering experiments of de Bergevin and Brunel [18]. In principle x-ray diffraction is also capable to collect many reflections and solve magnetic structures, but its main strength now seems to be the measurement of few reflections in order to uncover a key property of the system, such as the correlation of structural, orbital and magnetic degrees of freedom, or significant high-order contributions to the magnetic moment.

For future instruments and also for present single crystal instruments user-friendly data acquisition and data reduction software is needed. Up to now such software was usually written rather by beam-line scientists, then by software developers and it was the instrument/facility specific. Presently we observe and endorse the effort of neutron facilities to join forces and design new common software based on scientific and programming state-of-art developments, allowing for the common data reduction and output in the standard agreed formats. The best example is the Mantid project [19].

3. Software for magnetic structure solution

Research of magnetic structures has a smaller user- and consequently developer- community compared to ordinary structural crystallography, so the variety of the software for the magnetic structure solution is more restricted. The best developed software packages are Fullprof, Jana and GSAS. The primary design of such programs has been usually pivoted by a single outstanding scientist and there is a danger that these tools would not be maintained or further developed when the leading scientist will retire. Therefore the need of a joined initiative of the whole magnetic diffraction community emerges to ensure the sustainment of this precious heritage. We should support and encourage young scientists developing their own new programs, as for example *mag2pol* written by Navid Qureshi [20] or *spinvert* by Joseph A. M. Paddison [21].

4. Greater scope and improved accessibility of known magnetic-structure data

With the improvement of the quality of experimental data, the variety of the tools for symmetry analysis and the availability of various software for magnetic structure determination, the rate of the number of determined magnetic structures is steadily increasing. It is estimated that more than 5000 magnetic structures have been published up to now. However, until recently the lack of the standards for the description of magnetic structures have precluded not only the development of an appropriate computer database, but also an unambiguous communication of many of them. In order to palliate this situation, one of the most important aims of the Commission on Magnetic Structures created by the IUCr in 2011 has been the development of standards for the description and dissemination of magnetic structures. The important breakthrough in this aspect has been the development of the magCIF format by the commission under the direction of Branton J. Campbell and the supervision of the IUCr Committee for the maintenance of the CIF standard (COMCIFS). This official extension of the so-called Crystal Information File (CIF) format has rapidly been implemented in most of the available tools for magnetic structure determination, analysis or visualization. This faciliates a standard and unambiguous form for the report, communication, storage and retrieval of the results of magnetic structural research. The magCIF format uses in a systematic standardized way and in a form analogous to ordinary crystallography the symmetry constraints provided by the magnetic group for a simple and unambiguous description of the magnetic structure, restricting the listing of magnetic moments (or their modulations in the case of incommensurate structures) to an asymmetric unit. This has been the basis of the recently created database MAGNDATA [22, 23], from which, at the moment, more than 600 different published magnetic structures, including incommensurate ones, can be retrieved, visualized and downloaded as magCIF files.

Presently the magCIF format is restricted to magnetic structures described under their symmetry group, a MSG (magnetic space group) in the case of a commensurate structure, or a MSSG (magnetic superspace group) in the case of an incommensurate one. Representation analysis lacks at the moment a comparable standardization. A coming project of our commission is therefore to develop an additional extension of the CIF format for symmetry modes described by irreducible representations. This will enable to achieve a similar degree of standardization and disambiguation when magnetic structures are described or analyzed using representation analysis, and in particular when both magnetic group symmetry and representation analysis are applied together, which in fact, in our view, is the most efficient approach, and will become in the future the most widely used method.

5. New basic and applied science involving magnetic degrees of freedom

The main motivation of the research of magnetic structures is the search of new materials with interesting physical properties. Often such nontrivial properties arise due to the correlation of structural, magnetic and orbital degrees of freedom.

Recently multiferroic materials, where ferromagnetic, ferroelectric and often also ferroelastic orders are coupled, attracted considerable attention [24] and symmetry-based computational tools were developed for the easy prediction of the new candidates [25]. Exploring of multipolar orders in *d*- and *f*-electron systems, such as long-studied hexaborides [26], newly proposed pyrochlores and spinels [27] or zero-magnetization diamond-structure alloys [28], gains presently renewed interest. Distribution of unpaired (magnetic) electrons in an atomic shell might be more complex than envisaged by the dipolar approximation and quadrupolar, octupolar, toroidal or other higher orders might exist. Theoretical predictions should direct the experimental search for such novel orders.

Nowadays the concept of multipole is extended to the magnetic clusters, and is now named as "cluster multipole" [29]. It becomes more and more clear that such cluster multipoles can act like atomic multipoles, giving rise to intriguing couplings to external electric fields and/or external electric currents. The room temperature anomalous Hall effect in the coplanar antiferromagnet Mn_3Sn [30], and current induced switching of antiferromagnetic order (Edelstein effect) [31] are the two recent examples. The determination of magnetic structures is the key to understand and rationalize such nontrivial couplings to the cluster multipoles.

The interest to quantum systems, topological nontrivial states, frustrated magnets including dipolar and quantum spin ices [32], shows endurance. Propagation of quasiparticles in quantum magnets, such as magnons, spinons and triplons, is closely related to the symmetry of the underlying crystal and magnetic structures. Recently, nonreciprocal propagation of quasiparticles is widely recognized in noncentrosymmetric magnets [33]. Such nonreciprocity is a key element to realize rectifier devices for magnon-based spintronic technology, and hence is actively investigated now.

Topologically nontrivial states and related singularities in k-space have been widely discussed in electronic systems, such as topological insulators, and Dirac and Weyl points. Such concepts are now applied to the quasiparticles in quantum magnets, such as Dirac magnons in Cu_3TeO_6 [34]. Appearance of such Dirac magnons is strongly restricted by the magnetic symmetry, and hence a well characterized symmetry-based magnetic structure information is the key to understand the topological nature of quasiparticles.

The quest for multi-k structures is now rising, as they are the prerequisite for the formation of skyrmion crystals. For a long time it was thought that only metallic MnSi and FeGe with the chiral space group $P2_13$ could host skyrmions [35], but this dogma was broken by the discovery of magnetoelectric insulator Cu_2OSeO_3 [36]. Now new systems with skyrmions manipulated by very low electrical currents at ambient temperature are searched for, as they have great potential as magnetic information carriers.

Research of thin films, nano- and other artificial magnetic structures is now boosted due to advances in instrumentation, importance for industrial applications and due to the emergence of new fundamental phenomena [37]. We expect new interesting topics in this research area expanding the horizon of magnetic structure research.

References

1. H. Heesch. *Z. Kristallogr*. **73**, (1930), 325.
2. N. V. Belov, N. N. Neronova, T. S. Smirnova, *Sov. Phys. Crystallogr.*, **70**, (1957), 311.
3. W. Opechowski and R. Guccione, *Magnetism*, edited by G. T. Rado and H. Suhl, Vol. 2A (1965).
4. J. M, Perez-Mato, J. L. Ribeiro, V. Petricek and M. I. Aroyo (2012), *J. Phys.: Condens. Matter* **24**, 163201.
5. H. T. Stokes and B. J. Campbell (2019), unpublished.
6. S. Alexander, *Phys. Rev.*, **127**, (1962), 420.
7. J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, and M.I. Aroyo,Annu. Rev. Mater. Res. 45 (2015), 13.1.
8. ISOTROPY Software Suite, iso.byu.edu.
9. D. B. Litvin, *Magnetic Group Tables* (2013), International Union of Crystallography.
10. V. Petrícek, J. Fuksa and M. Dusek, Acta Cryst. A 66, (2010), 649.
11. J. Rodriguez-Carvajal, *Phys.B: Cond. Matt.*, **192**, (1993), 55.
12. V. Petricek, M. Dusek, L. Palatinus, *Z. Kristallogr*. **229**, (2014) 345.
13. W. Sikora, F. Bialas, L. Pytnik, *J. Appl. Cryst.,* **37**, (2004), 1015.
14. A. S. Wills, *Physica B*, **276,** (2000), 680.
15. A. A. Coelho, J. S. O. Evans, I. R. Evans, A. Kern, S. Parsons, *Powder Diffr*. **26**, (2011) S22.
16. https://europeanspallationsource.se/instrument-technologies/detector-systems
17. https://europeanspallationsource.se/instruments/magic
18. F. de Bergevin, M. Brunel, *Phys. Lett. A*, **39**, (1972), 141.
19. http://www.mantidproject.org/Main_Page20. N. Qureshi, *Journal of Appl. Cryst.*, **52** (2019), 175.
21. J. A. M. Paddison, J. R. Stewart, A. L. Goodwin, *J. Phys.B: Cond. Matt.*, **25**, (2013).
22. S. V. Gallego, J. M. Perez-Mato, L. Elcoro, E. S. Tasci, R. M. Hanson, K. Momma, M. I. Aroyo, G. Madariaga, *J. Appl. Cryst.,* **49**, (2016), 1750.
23. S. V. Gallego, J. M. Perez-Mato, L. Elcoro, E. S. Tasci, R.t M. Hanson, M. I. Aroyo and G. Madariaga, J. Appl. Cryst. 49, (2016), 1941
24. P. G. Radelli, L. C. Chapon, *Phys. Rev. B*, **76**, (2007), 054428.
25. J. M. Perez-Mato, S.V. Gallego, L. Elcoro, E. Tasci, M. I. Aroyo, *J. Phys.: Cond. Mat.* **28**, (2016), 286001.
26. A. Koitzsch, N. Heming, M.Knupfer, B. Büchner, P. Y. Portnichenko, A. V. Dukhnenko, N. Y. Shitsaevalova, V.B. Filipov, L. L. Lev, V. N. Strocos, J. Ollivier, D. S. Inosov, *Nature Comm.*, **7**, (2016), 10876.
27. Y. P. Huang, G. Chen, M. Hermele, *Phys. Rev. Lett.*, **112**, (2014), 167203.
28. S. W. Lovesey, T. Chatterji, A. Stunault, D. D. Khalyavin, and G. vam der Laan, *Phys. Rev. Lett.*, **122**, (2019), 047203.
29. M. T. Suzuki, T. Koretsune, M. Ochi, and R. Arita, *Phys. Rev. B*, **95**, (2017), 094406.
30. S. Nakatsuji, N. Kiyohara and T. Higo, *Nature* **527**, (2015), 212.
31. P. Wadley, B. Howells, J. Elezny, C. Andrews, V. Hills, R. P. Campion, V. Novak, K. Olejnik, F. Maccherozzi, S. S. Dhesi, S. Y. Martin, T. Wagner, J. Wunderlich, F.

Freimuth, Y. Mokrousov, J. Kune, J. S. Chauhan, M. J. Grzybowski, A. W. Rushforth, K. W. Edmonds, B. L. Gallagher, and T. Jungwirth, *Science* **351**, 587 (2016).

32. M. J. P. Gingras, P. A: McClarty, *Rep. Prog. Phys*. **77**, (2014), 056501.

33. Y. Tokura and N. Nagaosa, *Nature Comm.* **9**, (2018), 1.

34. S. Bao, J. Wang, W. Wang, Z. Cai, S. Li, Z. Ma, D. Wang, K. Ran, Z.-Y. Dong, D. L. Abernathy, S.-L. Yu, X. Wang, J.-X. Li, and J. Wen, *Nature Comm.* 9, (2018), 2591.

35. S. Mühlbauer, B. Binz, F. Jonietz, C. Pfleiderer, A. Rosch, A. Neubauer, R. Georgii, P. Böni, *Science,* **323**, (2009), 915.

36. S. Seki, X.Z. Yu, S. Ishiwata, Y. Tokura, *Science,* **336**, (2012), 198.

37. A. Huon, A. V. Vibhakar, A. J. Grutter, J. A. Borchers, S. Disseler, Y. Liu, W. Tian, F. Orlandi, P. Manuel, D. D. Khalyavin, Y. Sharma, A. Herklotz, H.N. Lee, M. R. Fitzsimmons, R. D. Johnson, and S. J. May, *Phys. Rev. B*, **98**, (2018), 224419.