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# Magnetic crystallography comes of age

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The special issue of *Acta Crystallographica B, Structural Science, Crystal Engineering and Materials* on magnetic structures is a must-read for anyone interested in new developments in crystallography. Not only do the many articles cover all aspects of the current state of this burgeoning field, but those articles have been written in such a way that they can be understood and appreciated by all structural scientists.

The first study of a magnetic structure, MnO, was published 75 years ago (Shull & Smart, 1949; Fig. 1). Shull and Smart demonstrated that the ordering of magnetic moments could be observed by neutron diffraction because neutrons have a magnetic moment. The study, done at Oak Ridge National Laboratory (ORNL), also showed that the predictions of Néel (1948) about antiferromagnetism were correct. X-ray and neutron diffraction give the same unit cell for MnO above its Néel temperature; below that point the cell determined by X-ray diffraction changes little, but the volume of the cell determined by neutron diffraction doubles.

One of the papers in the special issue (Pomjakushin, 2024) reports a new study of the MnO structure at temperatures down to 2 K (Fig. 2). The careful description of the structure and its refinement provide a good example of how magnetic structures are determined today.

The group at ORNL soon published two more papers (Shull *et al.*, 1951*a*; Shull *et al.*, 1951*b*) on paramagnetic, antiferromagnetic and ferromagnetic materials. Early work with magnetic materials was reviewed by Wilkinson *et al.* (1961) and by Mason *et al.* (2013). Wills (2017) recounted the history of the field going back to Pierre Curie's understanding that a magnetic field is a special kind of vector, invariant under inversion (Fig. 3), later termed an axial vector by Woldemar Voigt (1910). The history of the development of magnetic space groups is described in Chapter 3.6 of Volume A of *International Tables for Crystallography* (Litvin, 2016).

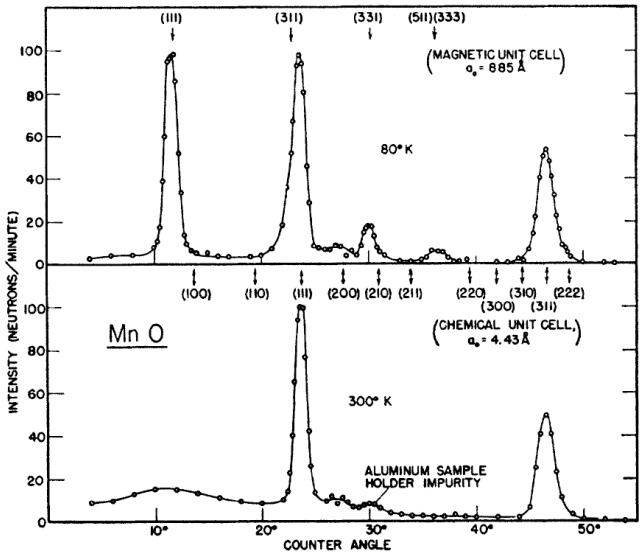
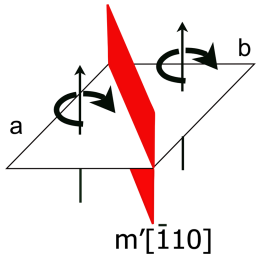



**Figure 1**
The neutron powder diffraction pattern of MnO at 80 K (below its Néel temperature of 115 K) and at 300 K ($\lambda$ is not given) taken from Shull & Smart (1949) with permission from the American Physical Society (2024). Some of the peaks in the low-temperature, magnetic form disappear above the Néel temperature.



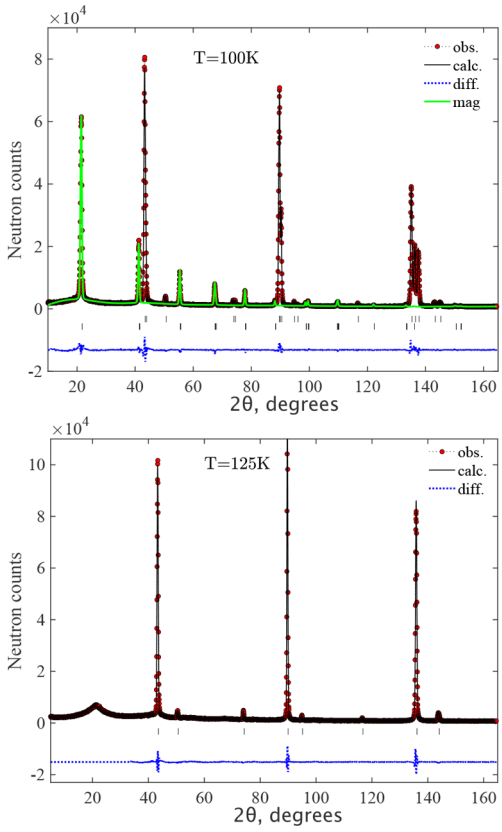



**Figure 2**
Part of Fig. 4 from Pomjakushin (2024) showing the neutron (λ = 1.886 Å) powder diffraction pattern of MnO at 100 K and 125 K (*i.e.* 10 K above its Néel temperature). The magnetic parts of the scattering are shown in green.

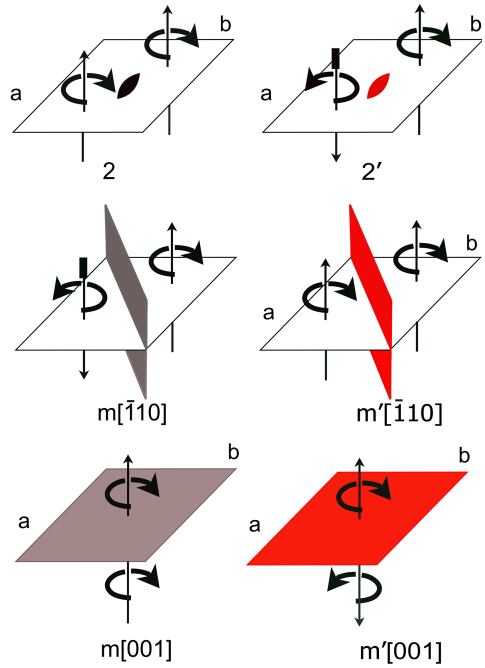



**Figure 3**
The effect of symmetry and antisymmetry operations (the latter primed and in red) on the magnetic-field vector. These drawings show that inversion generated by a twofold rotation followed by a perpendicular mirror (*i.e.* 2 followed by *m*[001] or 2′ followed by *m*′[001]) has no effect on a magnetic-field vector. Figure taken from Burns & Glazer (2013) with permission from Elsevier (2024).

Development of magnetic structure determination started slowly because the experiments still had to be done with neutrons,[1] the possible magnetic symmetries had to be tabulated, and language for describing the magnetic effects on the atomic positions had to be developed. Even so, increasing numbers of magnetic structures were determined, presented at meetings and published. The number is now in the thousands.

In 2011, the IUCr approved formation of the Commission on Magnetic Structures (the CMS). Some of the goals listed in the proposal to create the CMS were

(i) to establish standards for the description and dissemination of magnetic structures and their underlying symmetries,

(ii) to develop crystallographic information file (CIF) standards for magnetic structures and promote their use in crystallographic software,

(iii) to develop a database for magnetic structures based on the sharing of magnetic CIF files,

(iv) to cooperate with other IUCr Commissions in establishing and maintaining standards of common interest, such as magnetic symmetry-group tables, magnetic nomenclature and magnetic form factor data, and

(v) to encourage communication and cultivate consensus among research communities that have independently developed diverse approaches to characterizing and describing magnetic structures.

In September 2023, the CMS proposed a special issue of *Acta Crystallographica B* to report on their successes in meeting these goals. The proposal was accepted; papers started appearing in the August 2024 issue. This commentary will primarily focus on three papers of broad general relevance, while also referencing several others. The three papers are generous in crediting contributions and acknowledging the validity of opposing viewpoints.

## 1. Campbell *et al.* (2024). *A recapitulation of magnetic space groups and their UNI symbols*

The recent (Campbell *et al.*, 2024) and previous (Campbell *et al.*, 2022) articles proposing a unified set of symbols for magnetic space group (MSG) types also include a brief history of the development of those groups.

The first person to combine antisymmetry (or black–white or time-reversal[2] symmetry) with positional symmetry was Heesch (1929, 1930), who published in *Zeitschrift für Kristallographie*. While those papers did not attract much attention, Shubnikov's 1951 work (done independently) did, in part because of the book *Colored Symmetry* (Shubnikov & Belov, 1964) which contains English translations of some of the authors' papers.

[1] It was later demonstrated that magnetic ordering could also be studied with synchrotron radiation.

[2] For a magnetic structure, time reversal corresponds to switching the direction of all average magnetic moments.

The first full description of all 1651 MSG types seems not to have appeared until 2001 (Litvin, 2001; see its supporting information), although there had been much earlier reports about the groups (*e.g.* Belov *et al.*, 1957; Opechowski & Guccione, 1965) that included counts of the groups and symbols for them. Although the MSGs have yet to be included in any volume of *International Tables for Crystallography*, they are included in several software packages (*e.g.* Stokes & Campbell, 2010) and are freely available for browsing in the e-book by Litvin (2022) that follows the style of Volume A of *International Tables for Crystallography*.

Campbell *et al.* (2024) give easy-to-understand examples of the four kinds of MSGs.

(1) The 230 type 1 colourless groups that have no antisymmetry; *i.e.* the space group types given in Volume A of *International Tables for Crystallography*.

(2) The 230 type 2 grey groups in which all symmetry and antisymmetry elements are paired, with the members of each pair coincident.

(3) The 674 type 3 black–white groups in which half of the symmetry operations, but none of the translations, include antisymmetry.

(4) The 517 type 4 black–white groups in which a translation includes antisymmetry.

It is the type 4 groups that have caused the most problems in the past, problems that the proposed UNI system aims to resolve.

Because the type 1 groups have no antisymmetry, they are sometimes excluded from counts of the MSGs, in which case there are 1421 rather than 1651.

## 2. Rodriguez-Carvajal & Perez-Mato (2024). *Magnetic space groups versus representation analysis in the investigation of magnetic structures. The happy end of a strained relationship*

This very interesting and readable paper describes how the diverse approaches to describing magnetic structures have been reconciled. Some groups have used MSGs (or, in the case of an incommensurate structure, magnetic superspace groups, MSSGs) to describe their results. Other groups have used what has been called representational analysis (RA), which describes the magnetic structure in terms of irreducible representations (irreps) of the space group of the parent paramagnetic phase. (Examples of irreps familiar to most chemists are the rows of a point-group character table.)

The two approaches are now seen as complementary descriptions of a single symmetry-breaking process. A key step forward was the extension to magnetic structures of software tools using both symmetry groups and irreps; tools that were originally developed for the analysis of structurally distorted structures. For such structures the distortions could be described as a linear combination of irreps of the space group of the parent (aristotype) phase, with the space group of the distorted (hettotype) phase being related to the group of the parent phase by those irreps.

The paper by Rodriguez-Carvajal & Perez-Mato reviews the history of the two approaches, which goes back to the 1960s, when there was no compilation of the MSGs and RA was the only practical method for describing magnetic structures. Even though RA had been used in connection with space groups to describe mechanical distortions, the incorrect idea became established that MSGs and RA were competing rather than complementary approaches.

An MSG gives the symmetry constraints that must be retained in the magnetically ordered structure. The irreps identified by the RA method give the symmetry characteristics of the presumed pathway from the magnetically disordered (*i.e.* paramagnetic) structure to a more magnetically ordered structure of lower symmetry. The disordered paramagnetic structure is necessarily described by a grey MSG (and therefore by a standard SG), and the irreps are necessarily odd with respect to the antisymmetry operation. The MSG and RA approaches are complementary because specifying what symmetry is retained for all atoms (magnetic and not) need not be the same as saying what spin symmetry is broken during the transformation. The complementarity can be especially important if a key irrep is multidimensional.

An important part of the reconciliation was the recognition that there may be correlations in a magnetic structure that are not required by the MSG (just as an orthorhombic structure may be metrically tetragonal). This complication may arise, *e.g.* if the coupling between the magnetic ordering and the atomic positions is weak. It is now accepted that magnetic correlations not required by the MSG can be added manually.

The article by Nambu *et al.* (2024) presents both MSG and RA refinements of the magnet $Sr_2MnSi_2O_7$ (Néel temperature 3.7 K).

## 3. Perez-Mato *et al.* (2024). *Guidelines for communicating commensurate magnetic structures. A report of the International Union of Crystallography Commission on Magnetic Structures*

A database of magnetic structures is impossible without a standard format for the data. A standard format is also needed so that the different software packages for determination, visualization and analysis of magnetic structures can communicate. The magnetic CIF dictionary (magCIF) was approved by the IUCr in 2016 and has made possible the *MAGNDATA* database (Gallego *et al.*, 2016*a*; Gallego *et al.*, 2016*b*), which now contains more than 2000 structures.

A CIF for a magnetic structure is usually more complicated, even much more complicated, than are CIFs for non-magnetic structures, but the five software packages most commonly used for refinement (see below) all generate those CIFs. Examples of two such CIFs are included in the Perez-Mato *et al.* (2024) article; four more are presented with extensive comments in an accompanying paper (Damay, 2024).

The guidelines by Perez-Mato *et al.* (2024) list the items that should be present in a report of the determination of a magnetic structure so that it can be archived in a database. Items related to data collection, and many related to refine-

ment, are not discussed. The paper is designed for scientists who determine such structures, but it is also a good summary of the many problems inherent in presenting unambiguous results.

This 2024 paper argues that the MSG for the reported structure must be given along with atomic coordinates expressed in that basis, even if the analysis was done using the RA method (*i.e.* by determining the irreps of the parent paramagnetic phase that best describe the magnetic phase). This requirement guarantees that the report of the magnetic structure is complete in itself rather than depending on some other structure. (It is also possible to list alternative MSGs if they fit the data equally well.) Data items for describing the RA results are also available, in which case the irreps given need to conform to one of two standard labelling schemes. For some structures both the MSG and the RA results are necessary for a complete description. A procedure for generating a CIF from an RA refinement is also outlined.

Either the BNS (Belov *et al.*, 1957) or OG (Opechowski & Guccione, 1965) symbols may be used, but OG symbols are a problem for type 4 MSGs. It is expected that UNI symbols (Campbell *et al.*, 2022, 2024) will eventually become the norm.

Use of alternative space-group settings is much more common for magnetic structures than for non-magnetic structures. If a non-standard setting is used it should be related to the standard setting, preferably by giving both the equivalent positions and the transformation matrix (and any origin shift) relating the two settings so that a consistency check can be made.

Because magnetic ordering is usually weakly coupled to structural distortions, refinements often treat the magnetic and non-magnetic parts of the structure separately. Sometimes the positions of the non-magnetic atoms are taken from another study (*e.g.* of the parent phase at a different temperature) rather than being refined. It is argued that for all atoms the coordinates, even if approximate, must be given relative to the same unit cell so that the structural results can be used in, *e.g.* DFT calculations.

## 4. Software packages

The special issue will include articles describing the main software packages available for refining, analysing, and visualizing magnetic structures. Articles about *JANA2020* (Henriques *et al.*, 2024) and *GSAS-II* (Von Dreele & Elcoro, 2024) have already been published. Articles about the *ISOTROPY Software Suite* (Stokes *et al.*, 1995), the software on the Bilbao Crystallographic Server (Perez-Mato *et al.*, 2015), and *FullProf* (Rodríguez-Carvajal, 1993) will be published soon. All five packages produce magCIF files.

## 5. New structures and new science

The special issue will also include articles reporting diffraction studies of magnetic materials. The new study of MnO and NiO (Pomjakushin, 2024) has already been mentioned. A substantial paper (Calder *et al.*, 2024) on magnetic metal–organic frameworks (mMOFs) both reviews previous work and presents new results; that paper also discusses some aspects of data collection. Papers on the magnetic structures of $LuCrO_3$ (Muñoz *et al.*, 2024), ErGa (Cadogan *et al.*, 2024), and $Er_2CuMnMn_4O_{12}$ (Attah-Baah *et al.*, 2024) have also appeared.

## 6. Summary

Great progress has been made in the determination of magnetic structures since the groundbreaking work of Shull & Smart 75 years ago. Advances of the last 15 years or so include tabulation of the magnetic space groups, refinement programs for both powder and single-crystal data, an extension of the CIF format to cover magnetic structures, and the creation of a database that now has more than 2000 entries. After years of discussion the two approaches to refining and reporting magnetic structures are now understood as complementary; guides to interconverting their results are available. Incommensurate magnetic structures have been determined and reported. While determining, analysing, and reporting of a magnetic structure is very unlikely to ever become 'routine', the methods have now been standardized to the point that the focus can be on the implications of the structures rather than on their determination. The IUCr journals looks forward to publishing many more articles on the crystallography of magnetic materials [see *e.g.* the recent articles by Geers *et al.* (2024) and its commentary (Petříček & Henriques, 2024)].

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