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Validation of magnetic structures

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Abstract. Magnetic structures are the ordered arrays of magnetic moments that provide the basis for our understanding of the broad range of magnetic phenomena. Neutron diffraction provides what are arguably the most informative data on their nature. Given synthetic difficulties in growing single crystals, powder neutron diffraction is the technique of choice for the determination of the most significant qualities of magnetic structures. The literature reveals a lot of confusion over what magnetic structures are, both in the way that magnetic diffraction data are analysed and in mistakes that are commonly made when they are represented. In this article a brief overview is given about what magnetic structures are and what steps are required in order that they be validated as 'physically reasonable'. The discussion is limited to powder diffraction.

Magnetic structures – what they are

Magnetic structures may simply be defined as some periodic arrangement of atomic moments. There are many possible types of orderings: ferromagnetic, antiferromagnetic, canted, umbrella, sine, helical, cycloidal to name but a few.[1,2] The difference between these can be given simply in terms of the symmetry relations between the moments within the nuclear unit cell and the relation between moments in different nuclear unit cells. These two different types of symmetries will be discussed in turn using a language based on Bloch waves and representational theory.

Magnetic structures as Bloch waves

Bloch waves are the Eigenfunctions of the Hamiltonian with a periodic potential used to describe itinerant electrons. In real space they are described by the periodic repetition of a basis function. Similarly, magnetic structures are Eigenfunctions of the magnetic Hamiltonian and can be characterised using the same formalism.[1-5] A simple and general formalism for their description can therefore be constructed using the Fourier summation:

$$\boldsymbol{m}_j = \sum_k \sum_\nu \boldsymbol{\psi}_{ik}^\nu \exp(-2\pi i \boldsymbol{k} \cdot \boldsymbol{T}), \quad (1)$$

where the propagation vector $\boldsymbol{k}$ characterises the relation between the moment orientations of equivalent magnetic atoms in different nuclear unit cells and is defined with respect to the nuclear unit cell. $\boldsymbol{\psi}_i$ is the basis function of atom i labelled with the index ν. $\boldsymbol{m}_j$ is the magnetic moment on atom j The summation may be over several basis functions and propagation vectors of the first Brillouin zone. Expanding the exponential in equation (1) we obtain

$$\boldsymbol{m}_j = \sum_k \sum_\nu \boldsymbol{\psi}_{ik}^\nu \cos(-2\pi i \boldsymbol{k} \cdot \boldsymbol{T}) + i \sin(-2\pi i \boldsymbol{k} \cdot \boldsymbol{T}), \quad (2)$$

which demonstrates that the magnetic structures may be thought of as summed waves that propagate through the crystal structure: with out-of-phase real and imaginary components.

Translational symmetries – commensurate and incommensurate

An immediate consequence of the Bloch wave formalism is clarity about the differences between commensurate and incommensurate structures: commensurate structures correspond to simple fractional values where the imaginary part of the exponent is zero; structures that satisfy this condition will have simple periodicities and moments that are equal in magnitude. Structures that do not, will have non-zero imaginary components that cause the waves to be complex. In these cases the complex conjugate component must be added so that the magnetic moment is real. This conjugate term corresponds to the contribution with the propagation vector –k:

$$\boldsymbol{m}_j = \sum_k \sum_\nu \left(\boldsymbol{\psi}_{ik}^\nu \exp(-2\pi i \boldsymbol{k} \cdot \boldsymbol{T})\right) + \left(\boldsymbol{\psi}_{ik}^\nu \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{T})\right) \quad (3)$$

When indexing a magnetic diffraction pattern from powder data it is suggested that the points, lines and planes of the Brillouin zone be trialled sequentially as these correspond to magnetic structures with particularly symmetric translational symmetries.[6,7]

Symmetries within the unit cell

The symmetry operations of the nuclear space group, G_0, that leave the k-vector invariant form a subset, the little group, G_k, also called the space group of the propagation vector. The relationships between the orientations of moments within the nuclear unit cell are defined according to the symmetry operations of the little group, G_k The most elegant and mathematically simple way of describing these relations is to use functions that are symmetry adapted to the problem under study. These are the basis functions, ψ, and can be calculated using the projection operator technique from the irreducible representations (IRs) of the space group G_k. The generation of the IRs for this process will be commented upon later.

Sources of irreducible representations (IRs)

The source of IRs has a particular importance because at present there is no convention for their labelling or definition. They may be calculated *ab inito* using computer programs, commonly based on KAREP[9], or from tabulated works and their matrix representatives, or character tables or reference (in the case of tabulated works) must be given if they are to be verifiable. As the calculations are difficult and errors may not be apparent, Kovalev's tables [10] stand out as the reference of choice because they have been computer verified. The main difficulties associated with them arise from the not infrequent use of non-standard space group definitions, a historical relic from the time before the standardised International Tables were created. Both Kovalev's tables and a translation of KAREP are incorporated in the program SARA*h-Representational Analysis*.[6,7]

Common misconceptions and errors

Structures that do not propagate coherently

A survey of the literature shows that a key quality of magnetic structures that is commonly missed is their following of a wave equation that has a propagation vector. The role of $\boldsymbol{k}$ is to define the relative orientations of moments that are related by an integer primitive lattice translation. In centred cells, this means that moments related by the centring translations are also defined according to equation (1). It is important to note that two conventions for the propagation vector may become mixed unintentionally and erroneously, namely the definition of $\boldsymbol{k}$ with respect to primitive and centred reciprocal lattices. To save this confusion it is recommended that the k vector be given according to both these conventions when dealing with centred crystal structures. Taking the example of the BCC lattice where the moments related by the body centred translation are identical ($2\pi\boldsymbol{k}\cdot\boldsymbol{T}=0$) and reversed ($2\pi\boldsymbol{k}\cdot\boldsymbol{T}=\pi$), it is apparent that these situations correspond to the *k* vectors $\boldsymbol{k}$=(000) and $\boldsymbol{k}$=(½½½) with respect to the primitive setting as the body centred translation is a primitive lattice translation, and $\boldsymbol{k}$=(000) and $\boldsymbol{k}$=(100) with regards to the centred conventions, respectively. The phase relationship for the moments related by the body centring translation $\boldsymbol{T}$= (½ ½ ½) are often missed and ones that are inconsistent with equation (1) are the typical result.

The notion of a magnetic unit cell is partly responsible for this confusion. The above example is of two structures that have magnetic unit cells that are the same size with respect to the primitive unit cell, but are not centred. As explained earlier, the difference between commensurate and incommensurate structures is subtle, depending on the complexity of the exponential term in equation (1). The propagation vectors of centred cells are therefore to be considered with care.

Prejudice of trial structures

The symmetry types associated with magnetic structures can correspond to high dimensional spaces, frequently with 6 or more variables. They are consistent and follow the criteria for being Hilbert spaces. It is common for people refining magnetic structures to prejudice their choice of trial models according to simple symmetries under the symmetry operations of the space group, or perhaps local coordination directions. This course of action prevents the refinement from being a reasonable exploration of the data. If we define the symmetry ac-

cording to the IRs of G_k, it is easy to see these limitations. IRs may be of order 1 to 6. This means that IRs of order 2 characterise symmetries described using 2×2 matrix representatives. In the case of IRs of order 6, these matrices are correspondingly 6×6. It is evident that many of the allowed symmetries cannot be generated without considerable thought.

Different types of magnetic structure

The different types of magnetic structure may be classified according to the type of k-vector, be they commensurate or incommensurate, and the nature of the basis vectors, *e.g.* longitudinal sine structures correspond to incommensurate structures with basis functions that have only components perpendicular to the k-vector, and these lie along a single axis; helical structures similarly have basis vectors with components perpendicular to the incommensurate k-vector, but this time the real and imaginary parts are not-collinear; cycloidal structures are helical structures where the basis vector components are not perpendicular to the k-vector.[11]

Landau Theory – 'symmetry allowed' magnetic structures

Representational theory provides a general framework for the calculation and description of different magnetic symmetries. It takes the degrees of freedom associated with the magnetic structure, there are of course 3 of these for each magnetic moment in the primitive crystallographic unit cell, and classifies them according to symmetry spaces that may be defined by the linear combination of basis functions associated with an IR. It is Landau theory that now comes into play, defining what we commonly term as symmetry allowed magnetic structures. To a simple level approximation, Landau theory states that for a magnetic transition to be continuous it should involve only a single IR becoming critical. This means that the magnetic diffraction data of the corresponding phase may be described by the basis vectors of only a single IR. Analysis of the diffraction data then corresponds to the sequential exploration of the IRs, and in turn the linear combination of their associated basis vectors. As stated, this approximation is a starting point.[1, 11] Magnetic phase transitions may be first order and there are several occasions when the single IR rule can be broken. In the case of first order transitions, if the dominant term in the energy still follows Landau theory, it is often found that the single IR rule is followed: the first order term then modifies the structure, perhaps by bringing in three k-vectors into equation (1). Of course, if there are several sequential second order transitions each should involve a single IR, strictly an IR of the space group before the transition in question. Finally, mixing together contributions from IRs is allowed under particular circumstances, *e.g.* when the IRs are related by complex conjugation, or when inclusion of antiunitary symmetry brings two otherwise distinct IRs into the same irreducible corepresentation.[12]

Information required to define a magnetic structure

The above description on magnetic structures is intended to provide the information required to explain how magnetic structures can be validated as being physically reasonable and valid. This section will explicitly state the information required to enable this to be verifiable from

a literature perspective. No comment will be made on the correctness of the nature of the data analysis except a warning, that several trial structures may give identical powder diffraction patterns. Information required:

1. The propagation vector(s), ***k***, of the magnetic ordering, given in both primitive and centred settings for centred cells
2. The characteristic details of the IRs relevant to the refinement. These are either their character table, the matrix representatives themselves or explicit reference to some tabulated works, such as those by Kovalev
3. Definition of the basis vectors involved in the refinement. If the refinement was carried out in terms of components defined with respect to the crystallographic or other axis system, these should be brought into association with an IR so that the nature of the IRs involved in the transition is clear
4. Statement of which IR(s) describe the magnetic structure
5. The order of the magnetic phase transition and the expected applicability of results derived from Landau Theory, such as the single IR rule

An introduction to such refinement and a further discussion on the difficulties that are involved are given in [7].

Final words – unseen complexity

The information here represents the starting point for understanding what defines magnetic structure as being physically reasonable. There has been no space to go into other aspects of magnetic structures and symmetry, such as *S*- and *k*- domain structures, or multi k structures where the different values of ***k*** are not related by rotational symmetry. Also, information about these subtleties is completely destroyed by powder averaging and they are correspondingly indistinguishable according to powder diffraction, making their discussion outside the scope of this work. Not observing them should not to be mistaken for saying that they do not occur. These domain structures are degenerate and are therefore likely to occur whenever the symmetry of the magnetic structure is less than that of the paramagnetic state. Such domain structures should not be forgotten either as they may provide the key to understanding many subtle but important phenomena in magnetism. Interested readers are pointed to references [1] and [11] where they are discussed.

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