

Symmetry in the solid state; working beyond the space group†

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Central to the mechanics of modern crystallography is the notion of a unit cell. It has long been a dogma that crystals are made by repetition of these fundamental units in three-dimensional space. In the 1970s so called ‘aperiodic’ structures were found that could not be described by the framework of the crystallographic space groups. Rather, these structures were found to be periodic only in a space with greater than three dimensions and their description required crystallographers to employ coloured space groups or superspace groups. There are, however, fundamental limitations to a symmetry description that is based on a unit cell and simple crystallographic symmetry operations. A more general description of commensurate and incommensurate crystallographic symmetry can be constructed from representation theory, as has been developed to describe magnetic symmetry and ordering processes. This article reviews these different extensions to the crystallographic symmetry and details examples and limitations of space group theory.

Introduction

Modern crystallography, born from the pioneering X-ray diffraction experiments of von Laue *et al.*¹ and the Braggs,^{2,3} has at its core the notion that crystal structures are constructed by the periodic repetition of a unit cell in three dimensions. In 1973 de Wolff and Janner *et al.* showed that crystal structures existed that could not be described within this simple framework.^{4,5} They described the newly discovered crystal structures, exemplified by γ -Na₂CO₃, as being aperiodic in three dimensional space, but periodic in a higher dimensional space that included an additional coordinate, *colour*, and a propagation vector. This extension leads to the so-called ‘coloured’ and further to the superspace groups.

There are, however, important limitations associated with the types of symmetry that can be described in terms of space groups that are built up from symmetry operators and unit cells that prevents them from providing a general description

of symmetry in a crystalline solid. While the limitations of crystallographic space groups are clearly demonstrated by incommensurate structures, they do also apply to commensurate structures and it is certain that crystallography will need to develop out of the confines defined by a unit cell. An important parallel that aids the understanding of the limitations of space groups and how best to characterise and understand the symmetries of these higher dimensional symmetries comes from the field of magnetic crystallography, a discipline that was forced to grow beyond the standard crystallographic space groups by the microscopic picture of antiferromagnetic ordering first developed by Néel.⁶ Initially, extensions were made that were based on coloured space groups, just as is being done in current crystallography, but these can only be used to represent simple, frequently collinear, magnetic structures and more complex types of ordering were found, such as helical structures and ‘multi-*k*’ structures, that could not be usefully described within their formalism. In response, an alternative and more general formalism based on representational theory was developed and its application to magnetic crystallography will be reviewed briefly in this article.

† Electronic supplementary information (ESI) available: SARAH program suite. See <http://www.rsc.org/suppdata/jm/b4/b404156a/>



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Dr Andrew S. Wills graduated in 1993 from the University of Oxford with a first class degree in chemistry and went on to complete a PhD at the University of Edinburgh, under the guidance of Professor A. Harrison. He then spent a year working with Professor J. E. Greedan at McMaster University, Canada on the magnetic properties of the Li_xMn₂O₄ spinels before returning to Europe as a Marie Curie Fellow at the Commissariat de l’Energie Atomique, Grenoble in the group of Magnetism and

Neutron Diffraction. Subsequently, he worked at the Institute Laue–Langevin as an instrument scientist using advanced polarised neutron techniques to study magnetic ordering. He took up his current position as a Royal Society University Research Fellow in April 2002. Currently, he is involved in a wide range of topics that centre on answering questions in fundamental magnetism and developing, through polarised neutron scattering, magnetism as a tool for the study of chemical bonding. Dr Wills was awarded the 2004 PANalytical prize from the British Crystallographic Association for his work on magnetic symmetry and the 2004 B. T. M. Willis prize for neutron scattering from the Institute of Physics for his work on frustrated magnetism.

Frequent references are made to crystallography in order to reinforce the similarities between the mathematics of the two fields and highlight possible directions for crystallography to develop.

Extending symmetry to magnetic crystals and incommensurate structures

Coloured space groups

Extension of the space groups to magnetic structures was historically first done by the introduction of the non-positional parameter, colour. Defined as being either black or white, colour can be changed from black to white or *vice versa* by a new symmetry operation, I . Different types of coloured space groups are generated depending on whether I exists on its own or only in conjunction with the other symmetry operators of the space group and primitive lattice translations (Fig. 1). Such colourised space groups are of general use in solid state physics,^{7,8} but here we will focus on their application for magnetism and correspondingly I will be referred to as the time inversion operation, as the reversal of the current loop that creates a magnetic field reverses its direction. The notation for these coloured space groups was derived from that of the Hermann–Mauguin symbol for the normal Schönflies crystallographic space group by priming the operations that involve time reversal.^{9,10}

It is useful at this stage to revisit the requirements for a mathematical group, G , to be closed:

- G is a group is a set of elements: $A, B, C\dots$
- The product of two operations is a member of the group: $AB \in G$
- The product is associative: $A(BC) = (AB)C$
- There exists a unique identity: E
- Every element has a unique inverse: $AA^{-1} = A^{-1}A = E$

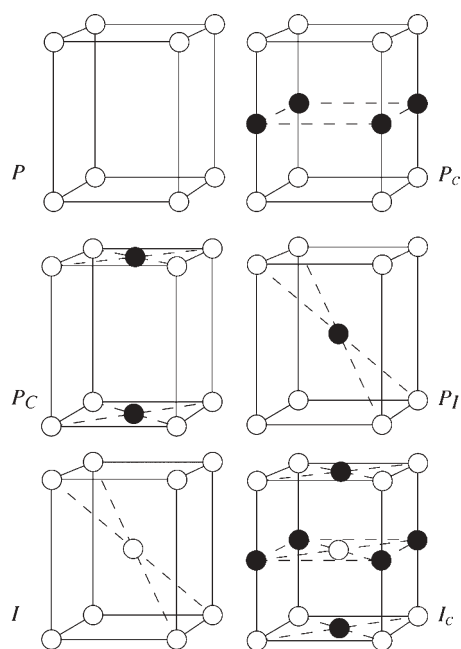


Fig. 1 The black and white tetragonal Bravais lattices.⁷

In the case of uncoloured space groups the symmetry operators in question can be described using 4×4 matrices and correspondingly the symmetry of a space group itself can be understood in terms of how different crystallographic positions are transformed by the application of these matrices.¹¹ It is often ignored that symmetry operations are in fact the simplest types of matrices that satisfy the above properties of a group and that other more complex types of symmetry are possible. Their properties are described by representational theory and will be described in the following section.

Representational theory and higher-order symmetry

Before moving on to introduce the different types of translational symmetry that are possible in a crystal it is useful to continue the discussion about the matrices which satisfy the properties of forming a group. These can be grouped together to form sets of matrices that make up a representation. In general there are a small number of irreducible representations which represent orthogonal symmetries and out of which any other representation, termed a reducible representation, can be formed. The matrices associated with the irreducible representations can have a dimensionality between 1 and 6.¹² In the case of one dimensional irreducible representations the value of the individual matrix representatives can have the value or either 1 or -1 . It follows that the simple types of symmetry described by space groups can be constructed from these one dimensional irreducible representations and it has been shown that coloured space groups themselves can be obtained simply by priming the operations that have matrix representatives with the character -1 .^{9,10} This process is general and if applied to the irreducible representations of non-zero propagation vectors, of the type detailed later, creates the superspace groups that are currently used to define incommensurate crystal structures.^{4,5}

The symmetry that is described by these higher-order irreducible representations, particularly those of order three and above, cannot be directly translated into the formalism of a space group. In magnetism these commonly involve structures in which the different magnetic atoms have moments with differing sizes. At first sight this may appear unphysical, but it must be stressed that the hypothesis that the moments on symmetry-related atoms be of the same magnitude is not always valid and partially ordered structures, such as that recently found in $\text{Gd}_2\text{Ti}_2\text{O}_7$, have been found (Fig. 2).¹³ Translating these ideas to crystallography appears first difficult as the obvious analogue to a partially ordered moment is a crystallographic site that is only partially occupied. This parallel is misleading as the symmetry properties of a magnetic structure are best defined not in isolation, but with respect to the structure before the ordering transition. Continuing this idea makes the crystallographic reference a structural phase transition. Now the crystallographic analogue of a partially ordered magnetic structure becomes clear: it is the result of a crystallographic distortion in which the equivalent positions of a crystallographic site move by differing amounts. To describe the final structure by space

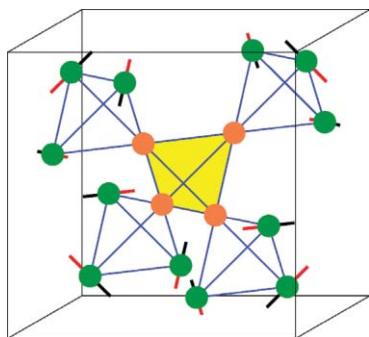


Fig. 2 The partially-ordered magnetic structure of $\text{Gd}_2\text{Ti}_2\text{O}_7$. Generated using four propagation vectors, the moments the central tetrahedron remain only largely disordered while those of the neighbouring tetrahedra order fully.¹³

group theory would require a unit cell that is either much larger or much lower in symmetry than the undistorted unit cell. Concomitant with these descriptions in defiance of Ockham's razor¹⁴ is an effective reduction of symmetry away from the true symmetry of the problem as can be properly described by representational theory.

The above discussion emphasises the concept that symmetry is not an absolute quality. Rather, it is defined with respect to a framework and as a consequence contains all of the limitations of that framework. In the case of space groups, the construction of a unit cell using a simple algebra of symmetry operations cannot well describe complex symmetry types, such as those associated with irreducible representations of order two and above. Attempting to do so destroys information because of the artificially low symmetry.

Translational symmetry; describing magnetic structures and displacive phase transitions using Bloch waves

In 1928 Bloch¹⁵ showed that the eigenfunctions of an electron moving through the periodic potential of a crystalline solid have the form

$$U_{\mathbf{k}}(\mathbf{r}) = U_{\mathbf{k}}(0)\exp(-2\pi i\mathbf{k}\cdot\mathbf{T}) \quad (1)$$

Where the exponential term relates the electronic wavefunction at position \mathbf{r} to that of a reference. The two positions are separated by the translation vector \mathbf{T} and the periodicity of the wave function is defined by the propagation vector \mathbf{k} . It is not surprising that the collective atomic displacements that give rise to a cooperative distortion or the ordering of moments to form a magnetic structure have the same form because they must obey analogous rules that reflect the symmetry of the crystal structure both before and after the transition. If we use $\psi_{\mathbf{k}}^j$ to represent an individual basis vector, j , which describes an atomic displacement or a magnetic moment, the total magnetisation or displacement, ψ , at a position \mathbf{r} is a symmetry adapted linear combination, SALC, that may in the most general case require several propagation vectors:

$$\Psi(\mathbf{r}) = \sum_{\mathbf{k}, j} C_{\mathbf{k}}^j \psi_{\mathbf{k}}^j(0) \exp(-2\pi i\mathbf{k}\cdot\mathbf{T}) \quad (2)$$

where C represents the mixing coefficient that defines the

contribution of the basis vector to the SALC. Expanding the exponential to give

$$\Psi(\mathbf{r}) = \sum_{\mathbf{k}, j} C_{\mathbf{k}}^j \psi_{\mathbf{k}}^j(0) \cos(-2\pi\mathbf{k}\cdot\mathbf{T}) + i C_{\mathbf{k}}^j \psi_{\mathbf{k}}^j(0) \sin(-2\pi\mathbf{k}\cdot\mathbf{T}) \quad (3)$$

reveals that magnetic structures or structure distortions can in their most general form be thought of as complex waves made up of real cosine and imaginary sine components.^{16,17}

The general description of magnetic structures and atomic displacements in terms of Bloch waves demonstrates that incommensurate structures of the type that are revolutionising crystallography are in fact no less conventional than commensurate structures, or even than those which do not break translational symmetry. They only appear unorthodox or 'aperiodic' when a description is attempted in terms of space groups and unit cells.

The actual value of \mathbf{k} is also significant because it corresponds to a vector in the reciprocal space of the crystal lattice before the transition. The different possible symmetries it can take then correspond to the symmetry points and lines of the Brillouin zone. The subset of space group symmetry operations that are compatible with the propagation vector, *i.e.* those that leave it invariant, form a space group, $G_{\mathbf{k}}$, and it is the irreducible representations of $G_{\mathbf{k}}$ that are used to classify the different types of symmetry compatible with the ordered phase. If $\mathbf{k} \neq 0$ the translational symmetry of the resultant structure will be different to that of the crystallographic space group, G_0 , before the transition and unless \mathbf{k} corresponds to a high symmetry point within the Brillouin zone, the number of symmetry operations in $G_{\mathbf{k}}$ will be less than that in G_0 , *i.e.* $n(G_{\mathbf{k}}) < n(G_0)$.

The mechanics of representational analysis

Calculation of the irreducible representations. The mechanics of how representational theory can be applied to a crystalline solid was worked out in the 1960s by a number of workers, such as Bertaut,^{18–21} Kovalev,¹² and Bradley and Cracknell.^{7,8} Despite the apparent elegance of the group theoretical equations their application is far from straight-forward. A large problem lies in the calculation of the irreducible representations associated with the point in the Brillouin zone that corresponds to the propagation vector \mathbf{k} . As already stated, these can have an order between 1 and 6 and their matrix representatives may be real, imaginary or complex. In addition to this obvious complexity, their calculation for points on the surface of the Brillouin zone is more involved than when the propagation vector \mathbf{k} lies within it. Historically there have been a number of sources of this information, but only one, the new edition of the tables of Kovalev,¹² have been verified by computer. This process was extremely important because it revealed the extent of the difficulties associated with calculating the different possible irreducible representations; over 500 errors were found. The importance of this collection is difficult to overstate because it has provided solid state scientists with reliable tables for what is arguably the first time.

It is unfortunate that the historical origins of these tables makes their application more arduous than it need be. The

crystallographic space groups for which they were developed have been redefined and extended by the crystallographic community over the years,^{22–25} most notably with the collation of the *International Tables for X-ray Crystallography* (1952)²⁴ and the First Edition of the *International Tables for Crystallography*²⁵ (1983). Creating a complete interface between the historic space groups of Kovalev's Tables and those used by today's crystallography was a necessary step for these tables to truly become accessible.²⁶

Symmetry of an atomic position. The next step in the process is to determine the symmetry of the atomic position that changes during the distortion or that carries the magnetic moment. Inspection of the *International Tables for Crystallography*²⁵ shows how the application of the different symmetry operations of a space group to a crystallographic position generates the other positions that are related to it by symmetry, the *equivalent positions*. A single crystallographic site can have between 1 and 48 equivalent positions and these are permuted under the symmetry operations of the space group. In our calculations it is no longer the symmetry of the space group that is relevant as the resultant magnetic structure or crystallographic distortion must be compatible with the periodicity of the propagation vector, \mathbf{k} . Consequentially, it is the symmetry of the space group of the propagation vector, $G_{\mathbf{k}}$, that is relevant and permutation of the equivalent positions under its symmetry operations that is required. The transformations of all the equivalent positions of each of the different crystallographic sites under $G_{\mathbf{k}}$ is embodied by the permutation representation, Γ_{perm} . The part of the permutation representation that contains the crystallographic positions occupied by the crystal structure or the magnetic moment bearing moments is relevant in the following arguments.

Symmetry of an atomic displacement or a magnetic moment. Atomic displacements and moments are described by two different classes of vectors. Atomic displacements are represented by polar vectors as they map directly the magnitude and direction of the displacement. Magnetic moments have a different symmetry that instead may be visualised as a charged particle that is moving in a loop. Such currents are left unaffected by the inversion operation and correspondingly the axial vector that represents them is also left unchanged by the inversion operation and that part of the composite improper rotations.

The transformation of a polar or axial vector under the different symmetry operations of $G_{\mathbf{k}}$ is termed the polar vector, Γ_{pol} , or axial vector, Γ_{axial} , representation respectively.

Projection of the basis vectors. It can be shown that the symmetry of the magnetic or structural phase transition, *i.e.* that of the permutation and the axial/polar vector representations together with the propagation vector, can be expressed in terms of the irreducible representations of the space group of the propagation vector $G_{\mathbf{k}}$, that is to say that the reducible representation which describes the phase transition can be decomposed, or expressed, in terms of the irreducible representations of $G_{\mathbf{k}}$.^{7,8} The actual basis vectors adapted to

the symmetry of the phase transition are calculated from the irreducible representations of $G_{\mathbf{k}}$ from Γ_{perm} and Γ_{polar} or Γ_{axial} by projection. The set of basis vectors associated with an irreducible representation make up a SALC that describes its symmetry. It should be noted that the individual basis vectors that make up the SALC have no particular symmetry significance and the same Hilbert space could be defined by different non-collinear basis vectors.

Basis vectors and Landau theory. The goal of our representational analysis is to calculate the SALCs that describe the symmetries of the possible magnetic or crystal structures. These SALCs are made up of linear combinations of basis vectors, $\psi_{\mathbf{k}}^j$, that have components on the different equivalent positions related by the symmetry operations of $G_{\mathbf{k}}$. The type of the resultant structure is characterised both by the propagation vector \mathbf{k} and the form of the different basis vectors in the SALC. In general each basis vector can be a complex vector that has non-zero real and imaginary components.^{16,17} In the case of an incommensurate structure, inspection of eqn. (3) yields the result that if the SALC is made up of collinear real and imaginary components, the resultant structure will be a sine wave. Conversely, if the real and imaginary components are non-collinear, the structure will be made up of out-of-phase cosine and sine components: a helix. The precise details of the helix, whether it is based on a circular or an ellipse will depend on whether the real and imaginary components have the same magnitude or not, respectively. In this way inspection of the different basis vectors that make up the SALC enables the symmetry type characterised by an irreducible representation to be visualised. Fig. 3 depicts some of the different types of magnetic structure. In a sense, these can be thought of as end members that differ in the form of the basis vectors, whether they are real or complex, collinear or non-collinear, and the symmetry of the propagation vector \mathbf{k} . Understanding the differences between possible structures in terms of the forms of the basis vectors and propagation vector involved simplifies greatly the description of possible orderings and consecutive phase transitions.

As has already been commented upon, this classification of symmetries and consequently structures according to irreducible representations is physically meaningful because it stems from the eigenfunctions of the Hamiltonian under question. While this division is always valid and provides a useful framework for describing structures, it is the application of the Landau theory²⁷ for a second-order, or *critical*, phase transition that defines what can physically be thought of as distinct magnetic or crystallographic structures. According to the Landau theory, a second-order phase transition should involve only *one* irreducible representation becoming critical. Consequentially, the resultant structure can be characterised by only one irreducible representation. This restriction is the key to the simplification of magnetic structures and crystallographic distortions that representational analysis allows; until now we have only used representations and their associated basis vectors as a general language with which to characterise symmetry-types, it is the application of Landau theory which requires that the symmetry type should

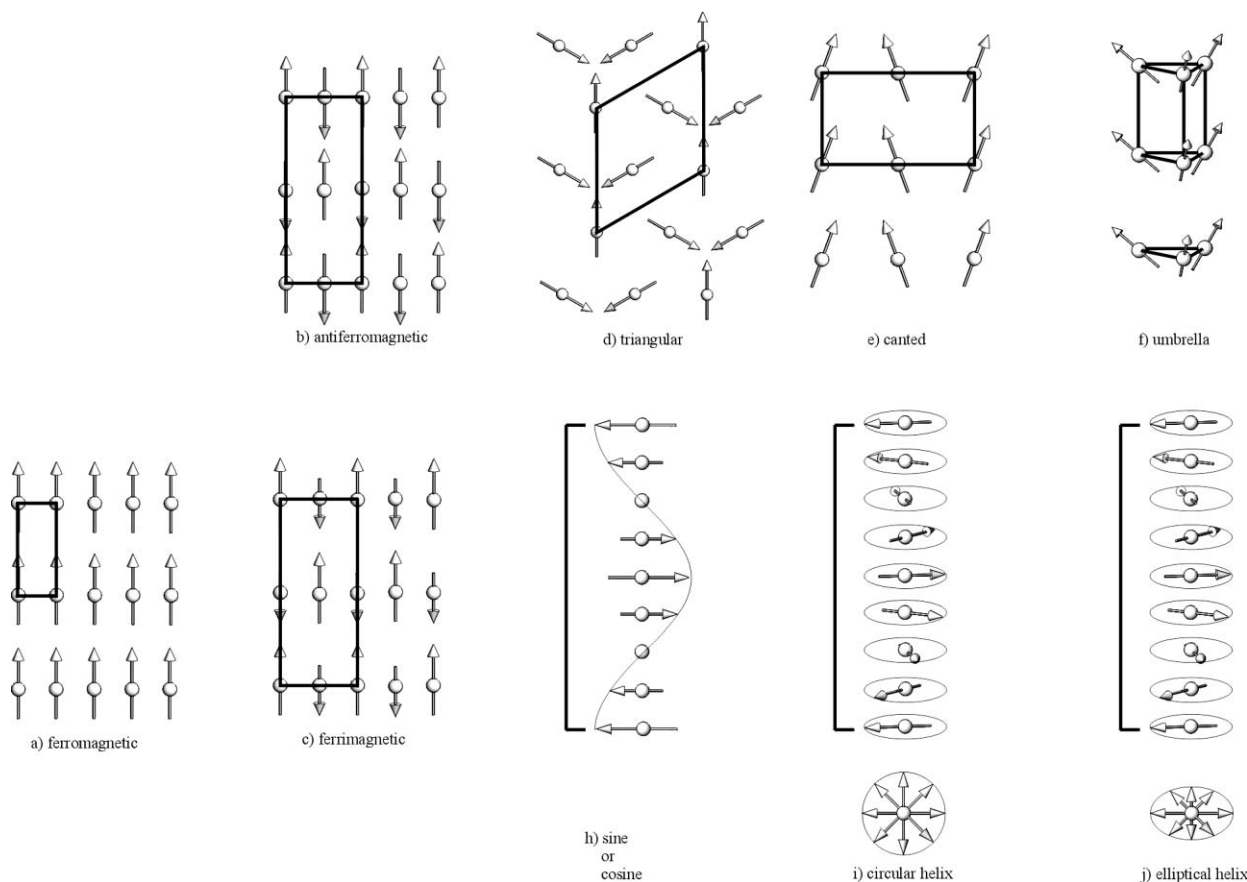


Fig. 3 Different types of magnetic structure that differ in the forms of the basis vectors and the propagation vector. The details of the magnetic ordering depend on the constituent terms of the electronic Hamiltonian. They can therefore be used to probe them directly.

correspond to only a single irreducible representation. Correspondingly, when a structure is refined it is sufficient only to refine the coefficients within the SALC that is made up of the basis vectors of a single irreducible representation.

The application of representational theory to the solid state

The importance of symmetry lies in its ability to facilitate our understanding or treatment of a problem. In a general sense it acts to simplify the degrees of freedom of a system into variables that are *fully adapted* to the problem, the mixing coefficients C^j of the SALCs, a step that makes tractable problems that might otherwise not be. Molecular orbitals, the effect of a crystalline electric field, ferroelectricity and vibrations are all examples of constructions and phenomena that rely on symmetry arguments in order to be understood. As well as providing a description of a phenomenon, symmetry creates a framework that enables better understanding of how perturbations can affect a system, *e.g.* selection rules in vibrational spectroscopy are based on whether the electric dipole moment operator has the same symmetry as the change in the vibrational wavefunction of the molecule or solid.²⁸

The concomitant improvement to our understanding that is a necessary result of discovering previously unknown

symmetry is largely the result of modern computer programs that provide the only mechanism by which the tedious calculations will actually be performed, such as SARA^h,²⁶ MODY²⁹ and BasiReps.³⁰ They are allowing the use of symmetry to again develop, as is well exemplified in the use of neutron spectroscopy to the study of lattice vibrations, phonons, and magnetic excitations, magnons. Neutron spectroscopy, also termed inelastic neutron scattering, was developed by Brockhouse, a work for which he was rewarded by a Nobel prize in physics in 1994. It is used to determine the spectra of lattice vibrations and magnetic excitations both as a function of their energy and their spatial periodicity, again characterised by a propagation vector \mathbf{k} . It can be argued that inelastic neutron scattering provides the most direct method by which the Hamiltonian of a system can be experimentally determined and the information that it has provided has shaped our understanding of the condensed matter. Despite this clear importance, the selection rules that characterise whether or not a lattice vibration is visible at a particular value of the scattering vector were unwritten until as recently as 1998.³¹ Indeed, the definition of these selection rules dispelled a common fallacy that there were no selection rules for inelastic neutron scattering. It is noteworthy that even today, the selection rules associated with inelastic neutron scattering are only partly formulated: those associated with the study of magnetic excitations, *magnons*, have yet to be derived.

Magnetism

Compatibilities between energy terms within the Hamiltonian; the example of the rare-earth nickel borocarbide superconductors.

An example of how symmetry can help us to understand the role of the different terms in the electronic Hamiltonian is provided by a study made of the rare-earth nickel borocarbides $\text{RNi}_2\text{B}_2\text{C}$.³² These materials display many of the physical properties that have captivated condensed matter research during recent years, *e.g.* square vortex lattices, superconductivity, heavy fermion ground states and metamagnetism. The particular interest in this family of borocarbides arose from all of these effects occurring within the same crystal type thereby allowing the interplay between a wide range of ground states and the different energy scales within the Hamiltonian to be examined and compared within the simplifying environment of the same structure-type. One major open question in the magnetism of these materials was why a range of different magnetic structures were observed when the translational symmetry of the Fermi surface, through an effect called ‘Fermi surface nesting’, would be expected to drive all the different members of this series into order with the propagation vector $\mathbf{k} = (0.55\ 0\ 0)$. As the detailed calculations of the electronic structures required to answer this question fully are computationally very expensive, and perhaps not even possible at present, a simple qualitative argument was desired. A particular energy scale that needed to be understood was the crystalline electric field which forces the magnetic moment, or spin, of the rare-earth ions to lie along particular local axes or in various planes. Symmetry calculations are computationally cheap and quickly revealed that in all cases where the directions of the atomic moments for the different symmetry-allowed structures associated with the propagation vector $\mathbf{k} = (0.55\ 0\ 0)$ were incompatible with the directions preferred by the crystalline electric field, a different propagation vector was found, one in which the directions of the magnetic moments allowed by symmetry match those preferred by the crystal electric field.

At first sight the efficiency of a simple study of the compatibility between the crystal electric field and the symmetry-allowed directions associated with the different propagation vectors is surprising because the crystal electric field of the majority of the rare-earths introduces terms of order three into the magnetic Hamiltonian which are incompatible with the energy requirements of the Landau theory and consequentially make the magnetic ordering transition first order. In so doing the restriction that the resultant structure corresponds to only one irreducible representation is removed. Despite this, in all cases examined the rule of ordering according to a single irreducible representation was found to be obeyed, demonstrating both that the crystal electric field is the dominant energy scale in the magnetic Hamiltonian and that it is responsible for driving the propagation vector away from that expected from the Fermi surface nesting, and that the transition still remains largely second-order.

Probing the Hamiltonian using Landau theory

Interest in magnetism comes not only from the control of magnetic properties themselves, but also from its use as a

probe of the electronic Hamiltonian: magnetic structures are a consequence of the interplay between the different possible terms. In the previous example symmetry was used to derive compatibilities between the energy terms, in this section the magnetic information will be used to provide evidence of additional contributions to the Hamiltonian.

Again the framework that will be used to understand the Hamiltonian comes from Landau theory. The rule that only one irreducible representation can be involved in a second order transition comes from the restriction that the energy terms which lead to the transition must remain invariant during the symmetry-breaking transition, that is to say they must be compatible with its symmetry. It can be shown that energy terms of odd order, commonly found to be those of order three, cannot be invariant and consequentially the transition they are involved in cannot be purely second-order, that is to say a first-order component is present.^{27,17} This leads to a relaxation in the rule that only one representation is involved in the transition. The observation that a single ordering transition leads to a magnetic structure that is described by several irreducible representations can therefore be taken as evidence of an odd order term in the Hamiltonian that couples the eigenfunctions associated with the different irreducible representations. An example of such a case is the heavy-fermion material UPt_3 , which crystallises in the hexagonal space group $P6_3/mmm$.³³ Below an ordering transition of $T_N = 6\ \text{K}$ a magnetic structure with the propagation vector $\mathbf{k} = (0.55\ 0\ 0)$ is observed. It is clear that in a hexagonal system the space group of the propagation vector $G_{\mathbf{k}}$ will contain one third of the symmetry operations in the space group, *i.e.* $n(G_{\mathbf{k}}) = n(G_0)/3$. In such cases group theory arguments show that third-order terms must be present in the Hamiltonian and consequently the transition cannot be purely second-order.

Other higher-order terms of even order are compatible with the Landau theory. Their effect will be to bring into the second-order phase transition orthogonal components by coupling them together. An example of this is multi- \mathbf{k} structures that are described by several symmetry related propagation vectors, such as the partially-ordered magnetic structure of $\text{Gd}_2\text{Ti}_2\text{O}_7$ shown in Fig. 2. It has been shown that structures made up of two or three symmetry related propagation vectors require large sixth order terms or fourth order terms respectively in the energy expansion.¹⁷ As these terms are frequently created by the crystalline electric field, observation of a 2 or 3 \mathbf{k} structure can in turn be used to deduce information about its details.

An example of new physics from new symmetry: the anomalous Hall effect

The use of symmetry theories that are based on representational theory has freed magnetism from the misplaced belief that magnetic structures are restricted to simple collinear geometries. This is leading to the discovery of *new* physics such as the anomalous Hall effect observed in the metallic ferromagnetic pyrochlores $\text{Sm}_2\text{Mo}_2\text{O}_7$ and $\text{Nd}_2\text{Mo}_2\text{O}_7$.^{34–36} The Hall effect signifies the presence of a coupling of charge transport to the fluctuations of magnetic spins, as is found in

the high- T_c cuprate superconductors, and is one of the fundamental mechanisms in the developing science of ‘spintronics’.³⁷ If the charge transport is characterised by a transfer integral, in the pyrochlores this integral is modified by the spin configuration and a phase must be introduced. This phase, termed the Berry phase, is related to the non-collinearity of the spin structure. This non-collinearity can be thought of as creating an effective magnetic field which gives rise to a transverse conductivity and hence the anomalous Hall effect. In greater detail, the magnetic order of the rare-earth moments form a *spin ice* system³⁸ in which the ferromagnetic exchange is frustrated by strong uniaxial spin anisotropy. The latter is the result of a crystal electric field that forces the magnetic spins to lie along the axes which point to the centre of the tetrahedra that make up the pyrochlore lattice (Fig. 4). Magnetic coupling between the rare-earth and Mo sublattices induces a spin ice-like state on the Mo sublattice, the electrons of which are partly delocalised to form the conduction band. Spin fluctuations then modulate the transfer integral and correspondingly link the magnetic ordering to the electronic transfer mechanism. It is a particular property of spin ice that it continues to fluctuate even at low temperature, in contrast with conventional materials, and so strong coupling is observed down to the lowest temperatures studied.

A similar anomalous Hall effect has been found in the magnetoresistive spinel $\text{Cu}_x\text{Zn}_{1-x}\text{Cr}_2\text{Se}_4$.³⁹ (where $0 \leq x \leq 1$) For $x = 0$ helical magnetic order characteristic of competing magnetic interactions is found below a transition temperature of ~ 20 K that changes gradually to becoming ferromagnetic as x is increased, until for $x \geq 0.3$ the spinel becomes metallic and localised magnetism is lost. Intermediate compositions possess a cone structure that can be thought of as being the result of a collinear ferromagnetic component along the direction of the propagation vector k and a transverse helical component. Again, it is believed that the anomalous Hall effect is a consequence of the Berry phase associated with the non-collinear magnetic ordering. The strong coupling between the charge transport and applied magnetic field (Fig. 5) that it creates is technologically significant because low magnetic fields give rise to a very large change in the electrical conductivity, exactly the effect required for the reading heads of magnet data storage devices.³⁷

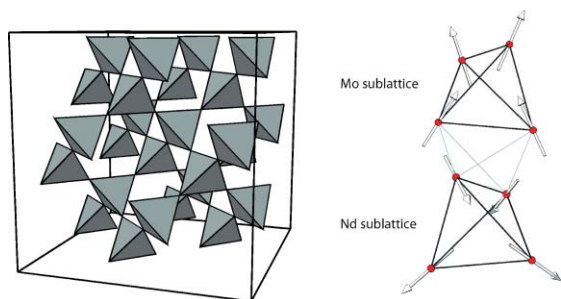


Fig. 4 The pyrochlore lattice made up of vertex sharing tetrahedra. The magnetic structure of $\text{Nd}_2\text{Mo}_2\text{O}_7$ showing how the spin ice state on the Nd sublattice (characterised by two spins pointing into and two spins pointing out of a tetrahedron) polarises the localised moments of the Mo sublattice.³⁴

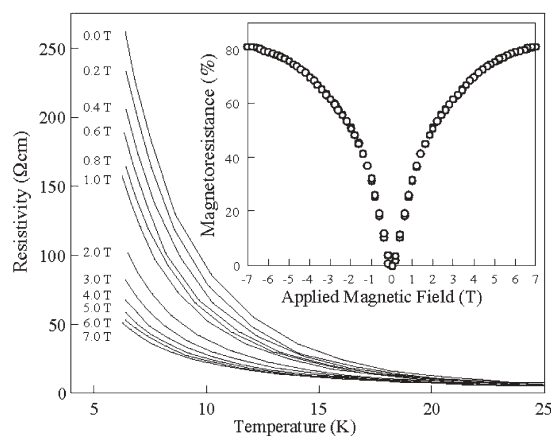


Fig. 5 Resistivity of $\text{Zn}_{0.95}\text{Cu}_{0.05}\text{Cr}_2\text{Se}_4$ below its antiferromagnetic ordering temperature as a function of applied magnetic field displays a remarkably powerful negative colossal magnetoresistance effect that is believed to arise from the non-collinear ferromagnetic ordering.³⁹ The inset shows the dependence of the magnetoresistance effect with field (-7 T to 7 T) at 3.2 K.

Advances in the application of symmetry to the solid state

It is often thought that the development of symmetry to the solid state ended with the *tours de force* made by workers such as Schönflies and Federov that gave rise to the crystallographic space groups. This is not true because, as we have argued, symmetry is relative to the framework within which it is defined and the observation of properties and effects that cannot be explained by current symmetry arguments leads to the formulation of new frameworks, just as magnetism was forced to develop using representational theory by the discovery of complex forms of antiferromagnetism. In a similar way, future developments in the parallel discipline of crystallography appear to be inevitable: there is no physical reason that prevents the complex structures allowed within representational theory from existing in the real world as well as the mathematical one of group theory. Crystallographic analogues of the sine and helix structures are already known, but at present these have only been examined in terms of superspace groups and the discovery of complex multi- k or partially-ordered structures that are based on the symmetries of higher-order representations is perhaps only a matter of time. These structures may feature periodicities, phonons or thermal parameters that appear unconventional when described within the reference of a space group and a unit cell or perhaps even representational theory, but are mathematically banal when explained within a more complete symmetry description. Until these frameworks are fully developed and their use is commonplace both the magnetic and chemical crystallographer must be alert to the possibility that their symmetry framework could hide a richer structure.

Postscript

It was with sadness that the author received news of the recent death of E. F. Bertaut during the preparation of this

manuscript. His work on the symmetry of magnetic structures provided the basis upon which much of our understanding of magnetic properties is founded.

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