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SARA*h*— webRepresentational Analysis

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This paper introduces the online software server SARA*h*—webRepresentational Analysis which replaces the previous Windows-versions of SARA*h*— Representational Analysis and SARA*h*—Refine, and related theory. The new suite of web apps carries out a range representational analysis calculations, including those based on the works of Kovalev, Bertaut, Izyumov, Bradley, Cracknell, Birman and Landau, for magnetic structures and electronic properties within frameworks based on the crystallographic space groups and point groups. Irreducible representations are sourced from the works of Kovalev, tabulated and computations are carried out on a server using Mathematica. The local user does not require a license for Mathematica and the calculations are provided free of charge. SARA*h*—webRepresentational analysis is available at: http://fermat.chem.ucl.ac.uk/spaces/willsgroup/

1. Introduction

While the use of representation theory was well established for the calculation of physical properties of atomic systems [Eckart (1930)] and crystals [Hund (1936)]; [Bouckaert, Smoluchowski & Wigner (1936)], such as the splitting and degeneracies of energy levels in materials with normal groups and black and white groups, it was the work of Kovalev (1963, 1964) and Bertaut (1968, 1971) that pioneered the use of basis vectors calculated by representation theory for the description of magnetic structures. Despite the subsequent successes of representation theory in describing and analysing magnetic structures, there was a gap between software that could perform representational analysis calculations, most notably MODY for DOS [Sikora (1994)], and magnetic neutron diffraction refinement codes which largely followed a crystallographic approach to magnetic structures, such as in GSAS [Larson & Von Dreele (1986)] where the relationships between the magnetic moments had to be defined in symmetry operations as either black or white, to encode the colour permutation of the (Shubnikov) magnetic space groups (MSGs). While FullProf [Rodriguez-Carvajal (1993)] had incorporated various descriptions for commensurate and incommensurate structures, such as using rotation matrices, integration of representational theory directly into its refinements was to come later [Rodriguez-Carvajal (2005)]. The typical situation resembled that of the 1970s [Izyumov & Ozerov (1970)] where refinement of a magnetic structure required a time consuming trial and error process of entering the symmetry constraints for each magnetic moment and testing against experimental data.

The original release of SARA*h*—Representational Analysis and SARA*h*—Refine [Wills (2000)] performed the calculations of Representational Analysis using irreducible representations calculated with a Visual Basic 6 translation of KAREP and then projected basis vectors following the methods of Bertaut and Izyumov. The results were integrated with the Rietveld analysis program GSAS using SARA*h*—Refine. Rather than refining magnetic moments directly, SARA*h* introduced a new protocol where the mixing coefficients of the basis vectors were used as refinement variables and applied global minimisation algorithms based on Monte Carlo and Simulated Annealing methods[1]. This change away from conventional least-squares minimisation combined with the typical reduction in the number of refined variables that came from representation theory, to allow the creation of maps of χ^2 against refinement parameters as a window to explore the refinement's modelling [Wills (2001)]. The functionality in SARA*h* then increased by incorporation of the computer files of loaded representations from Kovalev Tables as a source of irreducible representations (the 2K version); integration with the subsequent inclusion of basis vectors into FulProf [Rodriguez-Carvajal (2005)], and Topas. Routines were also developed to determine the values of k-vectors by Monte Carlo refinement of equal magnitude magnetic moments, without further symmetry constraint, for the various characteristic k-vectors of the Brillouin zone, a method named 'Brillouin zone indexing' [Wills (2009)]. SARA*h*'s development moved in 2018 to a web system and a new software framework based on Mathematica [Wolfram Research, Inc. (2024)].

Underlying the development and application of SARA*h* was the goal of linking the results of representation theory with refinements, and commonly used codes such as GSAS and FullProf. The web version of SARA*h* seeks not only to reproduce the original functionality; it seeks to extend it by collating a range of symmetry tools within a series of coherent workflows. An area that will be covered in a later report is the recent development of the SERENDIPITY protocol [Georgopoulou (2023)], which can determine stability conditions for an observed magnetic structure.

2. Software

The calculations in SARA*h* are carried out on a local

[1] SARA*h* takes its name from the combination of *S*ymmetry *A*nnealing and *R*epresentational *A*nalysis

server using Mathematica. The web interface takes in user data, performs the relevant calculation and then returns the output for display. This is preferred over the application of a database for flexibility and future development, but user requests do take longer because of the computational overheads. There are no separate programmes as part of SARA*h*. Instead, web apps are formed that direct and integrate the flow of various routines towards tailored goals and these flows will be a particular feature of the development. SARA*h*—webRepresentational analysis is freely available at: http://fermat.chem.ucl.ac.uk/spaces/willsgroup/

3. Application of Kovalev's Tables

This section introduces the main tables that are available in the English versions of Kovalev's published tables [Kovalev (1965), (1993)] and via SARA*h*, though it should be noted that Kovalev's initial collection of *Irreducible Representations of the Space Groups* was published earlier in Russian [Kovalev (1961)]. At the moment the calculations are focussed on the commonly found situation where there is a single k-vector and full-group method has not yet been integrated. The tables do contain more information than presented here and in future developments more data will be presented.

3.1. Irreducible representations of the little group $G(\mathbf{k})$

For each Bravais lattice, Kovalev's tables list a set of characteristic vectors[2], $\mathbf{k}$, within the first Brillouin zone (BZ). Taking G to be a crystallographic space group with symmetry operations $g = \{h \mid \mathbf{t}\}$, where g involves a (proper or improper) rotation h and a subsequent translation $\mathbf{t}$, the set of all the rotation operations h form the point group $\hat{G}$. Application of $\hat{G}$ to $\mathbf{k}$ transforms the vector into a number of vectors in reciprocal space with equal modulus. The set of operations $h \in \hat{G}$ with matrices $\mathbf{R}_h$ that leave $\mathbf{k}$ invariant within a reciprocal lattice translation:

$$\mathbf{k}' = \mathbf{k}.\mathbf{R}_h + \mathbf{K}, \tag{1}$$

form a subgroup $\hat{G}(\mathbf{k})$ of the point group $\hat{G}$ that is termed the point group of $\mathbf{k}$, the little-point group of $\mathbf{k}$ or the little co-group $\hat{G}(\mathbf{k})$ of $\mathbf{k}$ [Aroyo and Wondratschek 1995]. As this point group is defined up to an equivalence in $\mathbf{k}$, it may contain more operations than the isotropy group of $\mathbf{k}$ [Tolédano & Tolédano (1987)], which consists of those operations that leave $\mathbf{k}$ unchanged and the two constructions should be differentiated. The set of k-vectors, distinct up to the equivalence equation, generated by application of $\hat{G}$ to $\mathbf{k}$ forms the star of the propagation vector:

$$\{\mathbf{k}\} = \mathbf{k}_1, \mathbf{k}_2, ...\mathbf{k}_n \tag{2}$$

The subgroup of G consisting of elements, $h \in \hat{G}(\mathbf{k})$, whose rotation parts leave $\mathbf{k}$ unchanged or invariant up to this equivalence, forms the little group of the vector $\mathbf{k}$, denoted as $G(\mathbf{k})$. This subgroup is fundamental to the application of group theory to problems in condensed matter physics, including the description and analysis of magnetic structures. As the irreducible representations of $G(\mathbf{k})$ depend on the numerical value of $\mathbf{k}$, some attempts at tabulations made in the literature are quite voluminous, for example the tables of Miller & Love (1967). In a remarkable *tour de force* to reduce such tables to a core, Kovalev (1961) instead took advantage of a construction developed by Lyubarskii (1960) and presented the matrix representatives of the so-called weighted or loaded representations, $\hat{\tau}_p(h)$ of $\hat{G}(\mathbf{k})$ that are used to construct the small irreducible representations $\tau_{\mathbf{k}p}(g)$ of $G(\mathbf{k})$ according to the equation:

$$\tau_{\mathbf{k}p}(g) = \mathrm{e}^{-2\pi i\mathbf{k}.\mathbf{t}}\hat{\tau}_p(h) \tag{3}$$

Here the index p labels the irreducible representations. In applying Eq. 3, the loaded irreducible representations have the necessary mapping with the rotations of $\hat{G}(\mathbf{k})$ but for non-symmorphic groups are not the irreducible representations of the point group themselves. Where the space group operations used in Kovalev's tables do not match the cell choice and settings currently used in the International Tables-A, transformations of the symmetry operations and k-vector are performed [International Tables for Crystallography (2005)] by SARA*h* to enable their use. Tables of the irreducible representations of these groups $G(\mathbf{k})$ are presented following a labelling scheme exemplified by 'k3t2',where 'k3' is Kovalev's index for the k-vector type and 't2' is the IR label. When working with magnetism and the simple groups, this label should be extended to 'mk3t2', where the prefix *m* indicates that magnetic structures break time-reversal symmetry. In his tables Kovalev refers to groups whose elements correspond to geometric rotations or operations as simple groups[3] to differentiate them from double groups where they are matrix-rotations.

When working with the irreducible representations of the space groups, it should be noted that the tables based on other sources, most commonly those based on [Miller, S. C. & Love, W. F. (1967)], such as available through the Bilbao Crystallography Server [Aroyo *et al.* (2006)] and Isotropy [Stokes *et al.* (2007)] may not feature identical irreducible representations as the space group settings, symmetry operations and k-vectors may differ.

3.2. Irreducible corepresentations of the little group $G(\mathbf{k}, \theta\mathbf{k})$

Antiunitary symmetry was integrated with representation theory by Wigner (1959) to introduce invariance with respect to the time-reversal $t \to -t$, or, as he thought more appropriate, 'reversal of the direction of motion'. The application of the time-reversal operation, θ, brings together stationary states Ψ and $\theta\Psi$ that have the same energy in quantum mechanics. Its applicability to classical physical systems or to spinless quantum theory comes via the operation of complex conjugation, *i.e.* $\theta = K$.

Using D to signify a corepresentation, Wigner's work leads to an algebra that follows from the properties of the unitary (g) and antiunitary (a) operations:

[2] The general k vector is added to Kovalev's selection as k_0.
[3] this term is also used for groups with no self-conjugate subgroups [Dresselhaus et al (2008)]

$$D(g_j)D(g_k) = D(g_i g_k), \quad D(g)D(a) = D(ga),$$
$$D(a)D(g)^* = D(ag), \quad D(a_j)D(a_k)^* = D(a_j a_k).$$

The importance of complex conjugate in the above equations led Wigner to name these extensions, 'corepresentations'. Within the application of representational theory to magnetic structures, these corepresentations are used with the direct product of the crystal space group G or point group with the group $\{E, \theta\}$. A similar direct product of the crystal space group with $\{E, R\}$ is used to form the grey magnetic space groups, though there time-reversal is the linear operation of moment reversal $R = 1'$. This shared construction shows that the $M(\mathbf{k}) = \{E, \theta\} \otimes G$ is a form of space time symmetry group [Birman (1984)], though one that is over an antiunitary group. Kovalev termed such antiunitary groups 'neutral groups', following the language of colour symmetry [Senechal 1983] and to distinguish them from MSGs. Unitary operations appear in corepresentations as a unitary subgroup, which has allowed a shortcut whereby some common properties may be determined without calculation of the corepresentations themselves, explaining the utility and importance of the irreducible representations of $G(\mathbf{k})$.

In Kovalev (1993), a process was laid out for the construction of the irreducible corepresentations of $G(\mathbf{k}, \theta\mathbf{k})$ from irreducible representations of the unitary subgroup $G(\mathbf{k})$ according to 2 variations:

Variation I. When $-\mathbf{k}$ is not a member of $\{\mathbf{k}\}$ the corepresentations are of type c and are over the neutral group $M(\mathbf{k}) = G + \theta G$. Taking the unitary and antiunitary operations as g and $a = \theta g$, respectively, the matrix representatives of the corepresentation are constructed from irreducible representation, Δ, and have the form:

$$D(g) = \begin{pmatrix} \Delta(g) & 0 \\ 0 & \Delta(g)^* \end{pmatrix}, \quad D(a) = \begin{pmatrix} 0 & \kappa\Delta(g) \\ \Delta(g)^* & 0 \end{pmatrix},$$

where for simple groups $\kappa = 1$ and for double groups $\kappa = -1$ (Section. 3.3).

Variation II. When $-\mathbf{k}$ is a member of $\{\mathbf{k}\}$, the corepresentation is over the group $M(\mathbf{k}) = G(\mathbf{k}, a_0) = G(\mathbf{k}) + a_0 G(\mathbf{k})$. Here, a_0 is an antiunitary generating element that plays two roles in the form of the irreducible corepresentations. It acts in Variation II to extend the group to include the antiunitary operations and is involved in relating the matrix representative of the antiunitary operation to that of a member of the unitary irreducible representation. This is particularly important in magnetic structures where time-reversal links orbits of atomic positions that are equivalent under G but are separated in $G(\mathbf{k})$. Through the given equations, its choice also defines the value of the auxiliary matrix β where relevant. The matrices for the unitary and antiunitary operations are given for 3 possible situations:

Type a. These contain only one irreducible representation, Δ.

$$D(g) = \Delta(g), \quad D(a) = \Delta(aa_0^{-1})\beta,$$

where β satisfies $\beta\beta^* = \Delta(a_0^2)$ and $\beta\bar{\Delta}(g) = \Delta(g)\beta$.

Type b. This involves the same irreducible representation of the unitary subgroup, Δ, twice:

$$D(g) = \begin{pmatrix} \Delta(g) & 0 \\ 0 & \Delta(g) \end{pmatrix}, \quad D(a) = \begin{pmatrix} 0 & \Delta(aa_0^{-1})\beta \\ -\Delta(aa_0^{-1})\beta & 0 \end{pmatrix}$$

with $\beta\beta^* = -\Delta(a_0^2)$ and $\beta\bar{\Delta}(g) = \Delta(g)\beta$.

Type c. Here two irreducible representations, Δ and $\bar{\Delta}$, that are not equivalent combine to form an irreducible corepresentation.

$$D(g) = \begin{pmatrix} \Delta(g) & 0 \\ 0 & \bar{\Delta}(g) \end{pmatrix}, \quad D(a) = \begin{pmatrix} 0 & \Delta(aa_0) \\ \Delta(a_0^{-1}a)^* & 0 \end{pmatrix},$$

In these, β is an auxiliary matrix which satisfies

$$\beta\beta^* = \Delta(a_0^2), \quad \beta\bar{\Delta}(g) = \Delta(g)\beta$$

Wigner's labeling of the types of corepresentations corresponds to Kovalev's classifications: type 1 (Variation II, type a), type 2 (Variation II, type b), and type 3 (Variation I and Variation II, type c). The present author believes that historical developments have resulted in a sometimes confusing literature on corepresentations. Interested readers are encouraged to consult [Frei (1966)] and [Birman(1984)].

When applied to the representation analysis of magnetic structures, consequences of the extension from irreducible representations to corepresentations are most commonly seen as being responsible for joining coincidences between eigenvalues. This occurs, for example, when type c (Variation II) irreducible representations come together to form a corepresentation that links under time-reversal the orbits of a crystallographic site that are disjoint under $G(\mathbf{k})$ [Radaelli and Chapon (2007)].

Tables of irreducible corepresentations formed from the irreducible representations of $G(\mathbf{k})$ are presented along with details of the a_0 and β-matrices, where used. To encourage consideration of the consequences of the phase relationships between unitary and antiunitary components, the antiunitary parts are presented with 0 and π phase shifts. θ is used in labelling of the antiunitary operation and the user should adjust this to K when relevant. Corepresentations are presented following a labelling scheme exemplified by 'ak3t2,', 'ak3t2+t4'; here 'ak3' is Kovalev's index for the k-vector type for the antiunitary group, there is no indicator for a double group so the group is simple, there follows labels for the simple group irreducible representations used in the corepresentation construction and these have the form 't2+t4' for variation II, type c and 't2x2' for variation II type b. This scheme will be extended to complete groups by changing IR labels to majuscules, and to double groups by inclusion of '†'.

3.3. Irreducible representations of the double-groups of $G(\mathbf{k})^\dagger$

The application of group theory to crystallography typically pertains to classical systems or quantum states with integer angular momentum quantum numbers. For species with half-integer angular momentum quantum numbers, such as electrons, rotation by 4π rather then 2π is required to reverse the direction of momentum [Bethe (1929)]. This necessitates an extension from conventional geometry (simple groups) to either double-valued representations of single groups or a doubling of the group with single-valued representations [Opechowski (1940)]. Information on the latter, and a process for forming double groups and their irreducible representations are in presented in Kovalev (1993). This begins from taking the Euler angles for each proper rotation, h and deriving a set of 'matrix-rotations' (u-matrices). Such a structure creates a fixed correspondence to the h rotations which allows the u-matrices, $u(h)$, to be labelled according to the rotational symbol h, and their negative $-u(h)$ as h^*. In this way, a simple group H with rotations $h_1, h_2, h_3, \ldots, h_n$ forms the double group H_u with the matrix-rotations $h_1, h_1^*, h_2, h_2^*, h_3, h_3^*, \ldots, h_n, h_n^*$. Irreducible representations of the double groups have the notable property of being either even, $\pi(h) = \pi(h^*)$, or odd, $\pi(h) = -\pi(h^*)$.

The multiplication table for the matrix-rotations of the crystallographic setting and the irreducible representations formed from $G(\mathbf{k})$ are presented. These irreducible representations fall into two categories— those of the simple group extended to the double group are labelled by τ, and those constructed from the loaded irreducible representations $\hat{\pi}(h)$ of the double group $H_u(\mathbf{k})$ according to:

$$\pi_{\mathbf{k}p}(g) = \mathrm{e}^{-2\pi i\mathbf{k}.\mathbf{t}}\hat{\pi}_p(h) \tag{4}$$

are labelled by π.

Only τ and π irreducible representations that are even and odd, respectively, have application to physical systems [Kovalev (1993)] [Dresselhaus *et al.* (2008)] and are presented following a labelling scheme exemplified by '†k3t2' and '†k3p1'; here †' indicates a double group, 'k3' is Kovalev's index for the k-vector type, and 't2' and 'p1' are IR labels for τ and π type irreducible representations, respectively.

4. Calculation frameworks

In addition to providing a web-based source of Kovalev's tables, expanded and tailored to the user's problem, SARA*h* performs calculations based on representation theory. While this technique is most commonly associated with the celebrated paper [Bertaut (1968)]; Kovalev (1963) extended Dzyaloshinsky's (1958) work to presented a clear and detailed methodology based on Landau theory, the application of local symmetry requirements, and the calculation of the thermodynamic potential (Section 4.3.3) in terms of invariant combinations of basis functions associated with the irreducible representations of the space group, $G(\mathbf{k})$ (Section 3.1):

$$\mathbf{\Phi} = \mathbf{\Phi}_0 + I_0(T-\theta)f^2(c_{i,\alpha}) + \sum_\alpha A_\alpha f_\alpha^4(c_{i,\alpha}) + \sum_\alpha A_\alpha f_\alpha^6(c_{i,\alpha}), \tag{5}$$

where f^2, f_α^4 and f_α^6 are invariants constructed from coefficients c_i of the basis vectors with components $\alpha = (x, y, z)$ that transform according to a compete irreducible representation of the group G (Section 4.2), θ is the transition temperature, and $I_0 > 0$ at the transition temperature. These calculations enabled the determination of phase diagrams of possible magnetic structures when the translation properties of the magnetic structure were the same as, or different to, those of the crystallographic structure. This was an important contribution that effectively combined Landau theory [Landau & Lifshits (1980)], magnetic symmetry and representation theory.

A notable difference between the methods of Kovalev and Bertaut was the former's focus on transformation of real magnetic moments under the magnetic symmetry while the latter made explicit use of a permutation representation and Fourier components made up of complex basis vectors.

4.1. The little group method— irreducible representations of $G(\mathbf{k})$

Curently, projection of the basis vectors for possible magnetic structures in SARA*h* follows the method of Bertaut and begins from the magnetic representation, Γ^{mag}, which describes how the magnetic moments at the atomic positions change under $G(\mathbf{k})$. This representation can be decomposed into irreducible representations of $G(\mathbf{k})$ according to

$$\Gamma = \sum_\nu n_\nu \Gamma_\nu \tag{6}$$

where for a group of order $n(G(\mathbf{k}))$,

$$n_\nu = \frac{1}{n(G(\mathbf{k}))} \sum_{g \in G(\mathbf{k})} \chi_{\Gamma^{mag}}(g) \chi_{\Gamma_\nu}(g)^* \tag{7}$$

The basis vectors associated with an irreducible representation are calculated using a projection operator:

$$\psi_\nu^{i\lambda} = \sum_{g \in G(\mathbf{k})} d_\nu^{*\lambda}(g) \delta_{i,gi}\, \mathrm{e}^{-2\pi i\mathbf{k}\cdot(\mathbf{r}_{gi}-\mathbf{r}_i)} \det(\mathbf{R}_h) \mathbf{R}_h \phi_\beta \tag{8}$$

that when applied to a set of trial functions ϕ_β, commonly:

$$\phi_1 = (1\,0\,0),\ \phi_2 = (0\,1\,0), \phi_3 = (0\,0\,1), \tag{9}$$

will project out a basis of the irreducible representation. Here, $\mathbf{R}_h$ is the rotational matrix of symmetry operation $g = \{h|\tau\}$, and λ is the element of the representation matrix. In SARA*h* the final basis vectors come directly from Equation 8 and are not adjusted by normalization of an orthogonalization process, such as the Gram-Schmidt algorithm.

There are three features of representational analysis of magnetic structures that are worthy of emphasis. Firstly, projection from an irreducible representation of dimension d can result in up to $3d$ independent basis functions. When $d > 1$, use of high symmetry combinations of these basis vectors can simplify the related analysis of possible magnetic structures (Section 4.2). Secondly, the basis vectors are Fourier components characterised by the propagation vector $\mathbf{k}$ and following Equation 8 can be complex. Thirdly, the magnetic structure moment can be constructed from a simple sum of the basis vectors associated with the required propagation vectors and representations, with the contribution from each basis vector ψ_i weighted by a mixing coefficient, C_ν, according to:

$$\mathbf{m}_j = \sum_{\nu,\mathbf{k}} C_\nu^{\mathbf{k}}\, \psi_{i,\nu}^{\mathbf{k}} \tag{10}$$

This simple summation contains some of the key flexibilities in the application of representation theory to magnetic structures. What is included in the summation is also the source of many the arguments and misunderstandings. A common fallacy that should be corrected is the belief that

Betaut's work restricted the basis vectors to a single irreducible representation— this view is incorrect as he carefully to signalled more sophisticated scenarios, noting '*If the spin components S^α and S^β belong to different irreducible representations Γ^α and Γ^β, the spin Hamiltonian must have terms of order four at least*' [Bertaut (1968)], in line with the arguments from Landau theory that follow in Section 4.3.3.

Where the refinement code is able to use complex basis vectors directly, as is the case in FullProf, there is no need to make the magnetic moment components real during the refinement. Instead, the basis vectors that correspond to $-k$ and the complex-conjugate representation may be added to Equation 10 after the refinement, with matched coefficients, to form the final magnetic structure of real moments. This can be done in FullProf.

4.2. Subgroups, stationary vectors, isotropy groups and order parameters

When the irreducible representation has dimension > 1, high symmetry basis vector spaces and related magnetic structures can be constructed by applying restrictions to the values of the mixing coefficients. These are commonly referred to as isotropy groups or stationary vector groups, and are an example of where commonality between the mathematics of representation theory and magnetic space groups allows their frameworks to be used together.

The application of these isotropy groups grew from the problem of determining the possible subgroups of a parent group. Inspection of an irreducible representation of dimension 1 gives all the symmetry operations that have a character of unity and can thus be combined to form a subgroup. Irreducible representation of dimension > 1 can also be used to find subgroups by looking at operations that leave a vector in irreducible representation space, $\boldsymbol{\eta}$ invariant:

$$\mathbf{d}(g)\boldsymbol{\eta} = \boldsymbol{\eta} \tag{11}$$

Here $\mathbf{d}(g)$ is the matrix representative of g. By suitable choice of $\boldsymbol{\eta}$, all subgroups associated with an irreducible representation can be determined. The lowest symmetry subgroup is termed the kernel, and the higher symmetry groups are called epikernels [Ascher, 1977]. To find the magnetic space groups associated with an irreducible representation, one can identify the operations that reverse $\boldsymbol{\eta}$ with the antisymmetric operations of the magnetic space group [Stokes and Hatch, 1988]. As magnetic space groups involve real atomic moments, the mapping is direct when an irreducible representation is real, but when the irreducible representation is complex and not equivalent to a real irreducible representation, the physically irreducible representation can be applied. These are formed using a block matrix structure of the direct sum $\mathbf{d}(g) \oplus \mathbf{d}(g)^*$. A further connection with representation theory is that the vector $\boldsymbol{\eta}$ is made from the coefficients in Equation 10. A form of $\boldsymbol{\eta}$ that corresponds to a high symmetry structure within the irreducible representation basis vector space, restricts the coefficients in the basis vector summation and so corresponds to particular moment directions in the magnetic structure.

Ascher (1966) conjectured that for a continuous phase transition between two phases with symmetries H and $L < H$, the symmetry of L is always a maximal subgroup of H. This provided a link between active representations and the possible group L, and can be thought of as a requirement that there are a minimum in the thermodynamic potential associated with a maximal isotropy group but not the kernel. Subsequently, Mukamel & Jaric (1983) provided the first couterexamples to this conjecture involving quartic terms, with more examples found later [Michel (1984)]. Despite these failings, maximal subgroups do continue to provide an excellent starting points for considering possible magnetic structures [Aroyo *et al.* (2006)], in particularly in quartic Hamiltonians.

In this section, stationary vectors in irreducible representation space were introduced as an abstract tool that can be used to determine subgroups and the respective values of high-symmetry mixing coefficients. They also have physical significance— in the Landau theory of phase transitions, they can define an order parameters of the expansion. Through this step, the mixing coefficients that construct a magnetic structure in Equation 10 can be related to polynomial invariants, stability conditions and coupling between irreducible representations. This then allows Laudau theory to restrict possible order parameters and, consequently, the mixing coeffcients (Section 4.3.3).

For each irreducible representation of $G(\mathbf{k})$, SARA*h* presents the various stationary vectors and the associated black and white point groups formed from the rotational parts of the operations in $G(\mathbf{k})$. This provides a simple symmetry description that can be applied alike to commensurate and incommensurate magnetic structures, and is one that will be expanded upon in future updates. The utility of isotropy and stationary groups is embedded into the integration with FullProf (Section 5) through the ordering of the basis vectors selection tables.

4.3. Magnetic structures that involve several IRs

4.3.1. Primary and secondary order parameters An important result of isotropy or stationary vector groups is that, while irreducible representations are significant because they correspond to orthogonal symmetry spaces, Landau theory allows coupling between them. This can occur, for example, when the same group appears in several irreducible representations or when there is a secondary order parameter. The strength of such coupling depends on the details of the exchange terms and those in the Landau expansion. Within the $G(\mathbf{k})$ framework, common stationary vector groups and group–subgroup relationships can be read from the SARA*h* output to direct which basis vectors should correspondingly be combined.

4.3.2. Exchange multiplets Exchange multiplets are not a form of coupling, but their consequences are often incorrectly interpreted as coupling, so they will be discussed here. Conceived by Izyumov *et al.* (1979), exchange multiplets are a method to recover the magnetic structures possible when spin-orbit coupling is weak, and so when the magnetic Hamiltonian is isotropic.

Their construction is essentially different from the spin groups originally developed by Brinkman & Elliot (1966) and championed by Opechowski (1986), where the symmetry operations that act on position are decoupled from those that act on the moment directions. Instead, for exchange multiplets, the isotropic structure is first considered as that which corresponds to scalar basis vectors, which as of course isotropic under crystallographic symmetry operations. The axial property of the moments is then introduced, which, in the presence of spin-orbit coupling, can cause the degenerate basis vector space of scalars to become split.

Mathematically, exchange multiplets are determined by first calculating the reducible scalar (permutation) representation, Γ^{perm} by taking an element g to be acting on atom j in the zeroth unit cell according to:

$$\Gamma_{ij}^{perm}(g) = \delta_{i,gj}\, \mathrm{e}^{-2\pi i \mathbf{k}\cdot(\mathbf{r}_{gj}-\mathbf{r}_i)}. \tag{12}$$

These matrices will have character

$$\chi^{perm}(g) = \sum_i \delta_{i,gi}\, \mathrm{e}^{-2\pi i \mathbf{k}\cdot(\mathbf{r}_{gi}-\mathbf{r}_i)}. \tag{13}$$

Γ^{perm} can be decomposed over the irreducible representations of $G(\mathbf{k})$

$$\Gamma^{perm} = \sum_\nu n_\nu^{perm}\, \Gamma_\nu \tag{14}$$

For each non-zero irreducible representation in this decomposition, the direct product is taken with the axial vector representation, $\tilde{V}$ and the result decomposed over irreducible representations of $G(\mathbf{k})$.

$$\Gamma^{perm} \times \tilde{V} = \Gamma^{mag} = \sum_\nu n_\nu^{mag}\, \Gamma_\nu \tag{15}$$

In so doing, this sequence creates separate insights while recreating the decomposition of the magnetic representation, whereas in Bertaut's method, the permutation and axial vector properties (with representations Γ^{perm} and $\tilde{V}$, respectively) are combined to make the magnetic representation, Γ^{mag} which is then decomposed.

The use of exchange multiplets reveals which irreducible representations contained in Γ^{mag} would be expected to be coincident when the spin-orbit coupling is weak — the splitting of these multiplets from the state of degeneracy due to spin-orbit coupling is analogous to the splitting of electronic quantum levels in when a magnetic field is applied. As alluded to earlier, there is no coupling energy involved in exchange multiplets and it instead a technique to recover the situation of an isotropic Hamiltonian.

SARA*h* displays the exchange multiplets together with the stationary vector groups to help inform how and under what circumstances irreducible representations may combine.

4.3.3. Application of Landau theory This section will focus on results relevant to the current implementation. Interested readers are pointed to excellent monographs such as Landau & Lifshits (1980), Lyubarskii (1960), Tolédano & Tolédano (1987), [Izyumov & Syromyatnikov (1990)] and [Bradley & Cracknnell (1972)]. Landau's theory of phase transitions is the main source of rules that attempt to direct possible magnetic orderings. These rules are derived as consequences from an expansion of the thermodynamic potential, $\mathbf{\Phi}$, in terms of a power series involving one or more order parameters.

When considering magnetic structures, the requirements derived from Landau theory are necessarily dependent on the approximations made in the series expansion, which begins with the lower and upper limits of the power index.

A simple requirement for a phase transition to correspond to a minimum in $\mathbf{\Phi}$ is that there are no terms of order 1. The minimal physical model from Landau theory then restricts the series to terms of order 2. This approach is applied in many works, though sometimes not explicitly which can lead to some of the confusion. A result from Landau theory from the order 2 expansion is that an invariant cannot be made from coupling non-equivalent irreducible representations, leading to what some refer to as the 'rule of a single IR'. Conversely, when a magnetic structure is observed that involves only a single irreducible representation, it may be supposed that the series is of order two.

As the upper limit is increased, this result may be replaced by other sets of requirements or restrictions. In this manner, Landau theory should not be taken as giving an unequivocal rule. Instead it gives restrictions that are relevant for a particular approximation of the series expansion. Whether a transition is required or assumed to be second-order (continuous) or first-order (discontinuous), is also of fundamental importance in Landau theory and may affect the results. However, care must be taken when assuming an order for a transition, as the Hamiltonian may lead to a magnetic structure that appears to follow the requirements of a second-order phase transition because the terms that require it to be first-order have consequences that are harder to observe.

4.3.4. Calculation of invariant polynomials Following the methodology of [Izyumov & Syromyatnikov (1990)] the invariant polynomials are constructed and presented for different values of the stationary vectors of the irreducible representations (Section 4.2), which we take as an order parameter in the expansion of the thermodynamic potential, up to order 6 in the power index, following Section 4.2:

$$\mathbf{\Phi} = \mathbf{\Phi}_0 + r_2\boldsymbol{\eta}^2 + r_3\boldsymbol{\eta}^3 + r_4\boldsymbol{\eta}^4 ... + r_6\boldsymbol{\eta}^6 \tag{16}$$

where $\boldsymbol{\eta}$ has components $\{\eta_1, \eta_2, \dots\}$.

Further, stability conditions are presented based on the thermodynamic potential having a minimum from the first derivatives ($d\mathbf{\Phi}/d\eta_i = 0$), the second derivatives ($d^2\mathbf{\Phi}/d\eta_i^2 > 0$) and the requirement that the value of $\mathbf{\Phi}$ be positive at large values of the order parameter. It is suggested that the restrictions from the first derivatives and to be positive definite be considered separately, as the magnetic structure involved may be metastable with respect to one or more of the coefficients.

The calculation of coupled order parameters using stationary vectors, via a reducible representation formed by combining irreducible representations, allow the determination of which irreducible representations and isotropy groups can combine at a magnetic phase transition, within the relevant approximation of the series expansion [Stokes & Hatch (1991)]. These have not yet been implemented in SARA*h*, and instead the results of calculations based on Kronecker powers are provided.

4.3.5. Decomposition of the Kronecker symmetrized power

Following Tolédano & Tolédano (1987), if a representation Γ is carried by the space ϵ, the symmetrized Kronecker power $[\epsilon^n]$ carries the symmetrized *n*th power of Γ, Γ^n. SARA*h* uses this simple result to calculate possible couplings between the irreducible representations that correspond to the primary and secondary order parameters, in the manner of a broad selection rule. Currently, these calculations assume the mixed invariant is formed from a primary-order parameter of up to a power of 8 and a linear term, *i.e.* the lowest order term, from the secondary-order parameter. Possible couplings may thus be determined by decomposing the symmetrized Kronecker power of an irreducible representation in $G(\mathbf{k})$ over other irreducible representations of $G(\mathbf{k})$. The relevant couplings are then tabulated. Details of the various polynomial invariants can then be calculated with reference to the results from Section 4.3.4.

Once the irreducible representations of the primary and secondary irreducible representation are identified, the decomposition of the symmetrized Kronecker powers can be used to identify the minimal model of a suitable invariant.

4.4. Combining irreducible representations under time-reversal–antiunitary theory

Information on corepresentations (Section 3.2) is included as part of the representational theory calculations. Further integrations into the calculations are ongoing.

5. Integration with refinement software

The web version of SARA*h* is integrated with FullProf, marking an initial development of a refinement workflow that allows experimental data to be refined from powder and single crystal neutron scattering diffractometers. This is achieved by running SARA*h* calculations, which launch a subsequent editor webpage for FullProf pcr files. This webpage contains summary results from the representational analysis calculations, including information on stationary vector groups and exchange multiplets. The basis vectors for each irreducible representation are tabulated, allowing the user to select those to be inserted into FullProf for refinement. Separate tables are presented for stationary vector groups that re laid out with maximal symmetry groups first to facilitate use of these results.

Once basis vectors are selected, the user can chose between creating a template phase, to be manually edited and incorporated into the FullProf pcr file, automatically inserting a tailored phase into the pcr file, or editing of a pcr file that has an existing magnetic phase. The latter allows a magnetic phase to be updated quickly by simply selecting the required basis vectors and launching the edit.

The generated pcr information defines the magnetic structure in terms of complex (or real) basis vectors, with initial positions for each orbit, and the k-vector used in the symmetry calculations. Lattice parameters, the profile function and instrumental parameters are taken from a crystallographic phase that matches the space group and atom positions used in the symmetry calculations.

6. Other symmetries— magnetic space groups, colour groups, spin space groups

Representation theory provides a general framework that underpins the analysis of physical properties and characteristics, such as magnetic structures. A key aspect of its flexibility is that a core set of irreducible representations can be expanded or reduced by introducing relevant symmetry operators through induction. This is exemplified by the extension of irreducible representations to corepresentations and restriction to a subgroup, such as the relationship between the unitary group of operations and the antiunitary group. With this in mind, the paramagnetic magnetic space groups (MSGs) are an extension of the crystallographic space group G made by direct product with $\{E, R\}$ to form the grey group G', and its subgroups. While MSGs are typically viewed as being formed of the operators themselves, the MSGs can also be viewed in terms of representation theory as corresponding to the identify representation of G' over the space of real moments [Bertaut (1968)]. This MSG representation may be irreducible or reducible over the irreducible representations of $G(\mathbf{k})$. It may also be reducible over the representations over more than 1 k-vector. Therefore, if the MSG is taken as the group to characterise the symmetry of a magnetic structure, there is a natural connection with representation theory.

Shubnikov's work [Shubnikov (1951), Shubnikov & Belov (1964)] triggered a lot of subsequent activity in developing of groups and constructs that could be applied as solutions to the problem of describing magnetic structures. The development to polychromatic groups [Belov & Tarkhova (1956)], and then to spin-space groups [Brinkman & Elliot (1966)], took place with remarkable speed [Zamorzaev & Palistrant (1980)].

In color groups the 2-value construct of the black and white colors of MSGs is generalised to being a permutation operation over a number of color values, p. In the P-symmetry groups each symmetry operation corresponds to a fixed color permutation: MSGs are P-symmetry groups [Koptsik (1988)]. Another type of color groups are the W-symmetry groups [Koptsik (1975)]. These have the characteristic that the color permutation is not fixed to a symmetry operation; rathe, the color permutation depends on the atomic position to which the operation is being applied.

The links between representation theory and these symmetry group are simply exemplified starting from the Fedorov group where real one dimensional irreducible representations have a one-to-one mapping to MSGs (2 color P-groups) formlized by the Indenbom-Niggli theorem[Niggli (1959), Indenbom (1959)]. The stationary vectors of multi-dimensional irreducible representations can be used to identify symmetric subgroups that correspond to MSGs, and more broadly, polychromatic-color groups of both P and W types. Additionally, exchange multiplets can be used to recover the symmetry of the magnetic

Hamiltonian that was the driving cause for the development of spin groups [Izyumov *et al.* (1979)].

It is noteworthy that the complementarity of these frameworks is not restricted to a simple mapping between groups and irreducible representations, but also can be deeper, for example when representation theory can be applied in the derivation of the various groups.

7. Integration with other software

Users are advised of the potential need to change settings in their web browser to enable the locally held pcr file to be read and updated with the new version prepared by SARA*h* and methods are given for several common browsers.

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