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THE SYMMETRY AND ANTISYMMETRY OF DISTORTIONS

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by

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ABSTRACT

This work is about symmetry. In particular, it addresses the symmetry of distortions. Any parameterized path through configurational space is a distortion (distortion, distortion path, and pathway are used synonymously in this work). This goes beyond just the typical use of the term distortion that describes a path connecting a high symmetry prototype structure to a lower symmetry distorted structure; for instance, the tetragonal PbTiO₃ structure is commonly described as a distorted cubic PbTiO₃ structure. In this work, a distortion is any parameterized path through configurational space, including the paths that atoms takes when hopping between sites in a crystal lattice, the pathways taking reactants to product in chemical reactions and conformational changes, the paths taken in domain wall, dislocation, and grain boundary motion, and many other things. Clearly, understanding these paths is very important for many physical problems, e.g. an example is given in Chapter 1 where ignoring the consequences of distortion symmetry could result in overestimating the activation barrier for diffusion by a factor of ~5X (see Sections 1.1.2, 1.2.3, and 1.3.2). Fundamentally, distortion symmetry works because it recognizes the separation of the configurational space from the parameter of the pathway (herein referred to as the distortion parameter, λ). This separation is something like the separation between time and space in classical mechanics and so λ is seen as a "time-like" parameter. Because of the distortion parameter's time-like nature, the time reversal operation has an analog that reverses the distortion parameter. This operation is called distortion reversal. Distortion symmetry comes from considering the conventional symmetry of the configurations along a pathway in conjunction with distortion reversal. The content of Chapter 1 is mostly independent of the other chapters and is written to be of interest to a more general audience than the others.

Distortion reversal and time reversal are independent antisymmetry operations and so motivate the listing of the types of double antisymmetry space groups described in Chapter 3. The mathematical tools necessary to determine the types of double antisymmetry space groups are discussed in Chapter 2. Chapter 4 describes how the idea of rotation-reversal symmetry led to the development of distortion symmetry.

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PREFACE

I started working with Venkatraman Gopalan in 2012 at the end of his Crystal Anisotropy class. Our collaboration began with a lecture he gave on rotation-reversal symmetry, or "rotosymmetry", and double antisymmetry. The topic of the lecture was from his then recent Nature Materials publication with Daniel B. Litvin titled "Rotation-reversal symmetries in crystals and handed structures"¹.

I was intrigued by the idea that there were symmetry groups that were not yet known. In particular, I was interested in a table like this (see Fig. 2a in Gopalan & Litvin's paper¹ for the original version):



This table divides the types of double antisymmetry groups, believed to be 17,807 in total at the time, into eight categories based on whether or not they contain inversion ($\overline{1}$), rotation reversal (1^{ϕ}), and/or time reversal (1'). There is an "x" for the number of MR groups indicating that the number was unknown. With my then relatively nascent understanding of symmetry, it seemed to me that these groups, and therefore the value of x, should be easy to determine and so I set about to do so and began the collaboration with Prof. Gopalan and Prof. Litvin that has culminated in this dissertation and the works it describes. It is only a slight overstatement to say that the initial motivation for my PhD dissertation was to solve for x.

Having solved this problem, it is now known that the correct version of the table looks like this:



So, it turns out x=4,225. Other numbers were also corrected and the total number of types of double antisymmetry space groups was determined to be 17,803, four fewer than previously believed.

Now, years later, seeing how naïve and limited my understanding of symmetry and group theory was when I started working on double antisymmetry, it seems quite remarkable that the project was so successful. Largely, I would attribute this success to the complementary skills and experience of the members of the collaborations I have been so fortunate to be a part of.

After completing the double antisymmetry space groups project (see Chapter 3), I was tasked with finding applications and experiments to test rotation-reversal symmetry. The concepts of rotation-reversal symmetry were found to have some significant problems and limitations (see Chapter 4). From working on these problems, distortion symmetry was discovered and developed (see Chapter 1).

The chapters are not given in chronological order in terms of when the works were performed. Chapter 1 describes my most recent work and provides motivation for understanding double antisymmetry space groups (Chapter 3). Chapter 2 is on normalizers which are mathematical "tools" used extensively in Chapter 3, although, chronologically, the work in Chapter 2 actually came after the work in Chapter 3 because the space group normalizers were already available. Chapter 4 describes the problems with rotation-reversal symmetry that motivated the development of distortion symmetry. Although distortion symmetry (Chapter 1) will likely make the largest impact, my work on affine normalizers (Chapter 2) and double antisymmetry groups (Chapter 3) is what I am most proud of from my graduate work and I am very thankful to have had the opportunity to work on these very unusual and fascinating projects.

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Chapter 1

Distortion reversal

Distortions are ubiquitous in nature. Under external perturbations such as stresses, fields, or temperature changes, atoms in a physical system reconfigure by following certain real space trajectories from their initial parent state to a distorted state; the collection of all such atomic trajectories describes a distortion. Here we introduce an antisymmetry operation called distortion reversal, 1*, that reverses a distortion pathway by reversing the trajectory of each atom. The symmetry of a distortion pathway is then uniquely defined by a distortion group involving 1*; it has the same form as a magnetic group that involves time reversal, 1'. Distortion symmetry has important implications for a range of phenomena such as diffusion, molecular conformational changes, vibrations, chemical reaction pathways, phase transitions, and interface dynamics. It can dramatically improve the speed and accuracy of transition state searches performed with nudged elastic band (NEB) calculations by symmetry-based approaches to computing minimum activation energy pathways and potentially quadrupling its overall performance.

Much of the material in this chapter is taken from a recently submitted manuscript titled "The Antisymmetry of Distortions" by myself (Brian K. VanLeeuwen) and Venkatraman Gopalan. As it is in the manuscript, this chapter is divided in a main text (the section that follows this one), the methods used to obtain the results shown in the main text, and a section with discussions and figures that supplement that of the main text.

1.1 Distortion symmetry: definition, examples, and applications

A distortion or distortion pathway refers to any one of the many possible paths between two or more states of a system. They are important for understanding chemical reaction kinetics²⁻⁶, phonon modes⁷⁻⁹, molecular pseudorotations and conformational changes⁴⁻⁶, diffusion¹⁰⁻¹³, the motion of interfaces such as grain boundaries^{14,15}, domain walls^{16,17}, and dislocations^{18,19}, and emergent phenomena in transient or metastable states that arise from a distortion of the ground state²⁰⁻²⁵. There is often a privileged point on a pathway that is extremal in energy. For stable phonons, this is the ground state; for unstable phonons, the parent structure; for reaction pathways, the transition state; and for phase transitions, the saddle point. The relative energy of this point corresponds to the activation energy in transition state theory^{4,26}. In many important pathways, it is found that the energies on either side of this privileged point are symmetric, e.g. when opposite sides are mirror images of each other. An antisymmetry operation named distortion reversal, 1* is introduced here to describe the complete symmetry of such pathways. When combined with conventional symmetry groups, it gives rise to distortion groups. The symmetry of a distortion pathway is uniquely described by a distortion group.

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Distortions, especially phonon modes, are sometimes studied using representation analysis⁷⁻⁹, through decomposition onto a symmetry-adapted basis using irreducible representations (irreps). The representation analysis of a distortion and its distortion symmetry are strongly connected through a correspondence between 1-dimensional real irreps and distortion groups, and they can each be used independently or in complementary ways. This is analogous to the relationship that exists between the representation analysis of a magnetic structure and its magnetic symmetry^{27,28}. In developing distortion symmetry, we discovered that a somewhat similar concept was introduced several decades ago in transition state theory in the limited context of reversing reactants and products in simple molecular reactions⁴⁻⁶. In this chapter, it is demonstrated that the concept of distortion groups is much more general, and can be used for studying "distortions" interpreted in a very broad sense. Further, they can predict the form of tensors that describe any property change of a system as a function of distortion.

The concept of distortion reversal is introduced in Figure 1-1a in a discrete system through three arbitrarily placed atoms (in red). The atoms then displace to their new positions as per the displacements shown as arrows. The structure in light pink is the result of displacing each position accordingly. The action of the distortion-reversal operation, 1*, on the distortion in Figure 1-1a is the reversal of displacements u_i of the atoms i (=1, 2, 3) to $-u_i$. Figure 1-1c depicts a parameterization of the atomic positions (r'_i) by a variable λ , *i.e.* $r'_i = r_i + \lambda u_i$, where $-1 \le \lambda \le +1$ and r_i are the positions at $\lambda=0$. The atomic trajectories in this

example are linear with respect to λ , but in general, they are allowed to be nonlinear. These displacements have been decomposed in Figure 1-1d into rotation ($u_{i,R}$, Figure 1-1e), translation ($u_{i,T}$, Figure 1-1f), scaling ($u_{i,S}$, Figure 1-1g), and deformation $(\boldsymbol{u}_{i,D}, \text{ Figure 1-1h})$, i.e. $\boldsymbol{u}_i = \boldsymbol{u}_{i,R} + \boldsymbol{u}_{i,T} + \boldsymbol{u}_{i,S} + \boldsymbol{u}_{i,D}$. This is analogous to the Helmholtz decomposition of continuous vector fields into components. This decomposition is not necessary for implementing 1*, but it is helpful to illustrate the relationship between 1*, and the rotation-reversal operation, 1^{Φ} , introduced by Gopalan and Litvin¹. While 1^{Φ} reverses the rotation component, $u_{i,R}$ (Figure 1-1e) to $-u_{i,R}$, it has no clear implications for the other components. This creates a problem in implementing 1^{Φ} , because it requires the identification of appropriate polyhedra within a structure that exhibit rigid rotations, but not the other components; the process for such polyhedral identification is non-unique, and often approximate in real systems. This is explored in more detail in Chapter 4. In this work, no such polyhedron is required to be identified in implementing 1* as seen from Figure 1-1a and b. Further, 1* reverses all the components of u_i , i.e. $1^*(u_{i,R}, u_{i,T}, u_{i,S}, u_{i,D}) = (-u_{i,R}, -u_{i,T}, -u_{i,S}, u_{i,D})$ $-u_{i,D}$), not just rotation, $u_{i,R}$, and in this sense, 1^{Φ} is a special case of 1^{*}, which is more general.





Three atoms are displaced to new positions in **a**. 1* reverses these displacements in **b**. The linear trajectories are parameterized by λ in **c**. In **d**, the displacements are decomposed into rotation (**e**), translation (**f**), scaling (**g**), and deformation (**h**).

Now several important observations are made regarding the distortionreversal operation, 1*. First, in addition to the ordinary space and time dimensions, a distortion has a time-like dimension that describes the extent of the distortion. This extra dimension is labeled λ . For a reaction pathway, this is the reaction coordinate; for a phonon mode, this is the amplitude; and for a phase transition, this is the order parameter. Note that for coordinates (r, t, λ) , spatial inversion, $\overline{1}$, reverses the position vector $\mathbf{r} \rightarrow \mathbf{r}'$, 1' reverses the time $t \rightarrow -t$, and 1* reverses $/ \rightarrow -/$. Secondly, an analogy to the time-reversal operation, 1' can be drawn from Figure 1-1. If λ is replaced with t, then the displacement vectors u are replaced with velocity vectors, v, and 1* is replaced by 1' between panels in Figure 1-1a and b. If the velocities were decomposed in a similar way as in Figure 1-1, the rotational component of this decomposition would correspond to angular momentum, and for charged particles, magnetic moment. Because it was inspired by the practice of applying 1' to reverse the localized magnetic moments of atoms (see Chapter 4), Gopalan and Litvin's rotation-reversal operation, 1^{Φ} , focused exclusively on the rotational component¹. Third, note that the action of 1* is well defined on any structure that is parameterized by λ , not just a system of discrete atomic positions and displacements. For example, in calculating ferroelectric polarization, the modern theory of polarization implicitly parameterizes the electronic wavefunctions of a system by λ by parameterizing the ionic positions and then calculating the ground state electronic structure for a series of steps between $0 \le \lambda \le +1^{29}$. On such a system, 1* has a well-defined action, even on the electronic structure that is only implicitly parameterized.

Fourth, note that most generally, any parameterized path through configurational space can be considered as a distortion, not just linear paths like the one shown in Figure 1-1; this is illustrated in the examples given later. Fifth, note that the symmetry of a distortion is *not* generally the symmetry of any particular static structure along the pathway; it is the symmetry of the entire distortion pathway, *i.e.* the full collection of structures from $\lambda = -1$ to $\lambda = +1$ and the parameterization. Generally, many different distortion pathways may be of interest between a fixed pair of static structures and these pathways may have different distortion symmetries.

1.1.1 The symmetry of the PF₅ pseudorotation

Figure 1-2 shows the pseudorotation distortion of phosphorus pentafluoride, PF₅, a well-known fluxional molecule. The ground state geometry of PF₅ has $\overline{6}2m$ symmetry. The distortion proceeds by the Berry mechanism⁵ where the pair of fluorine atoms on the high symmetry axis move down as another pair of fluorine atoms move up. The structure goes through an intermediate transition state with 4mm symmetry to a final state with $\overline{6}2m$ symmetry. Although this distortion is not a rotation, the final state is equivalent to the original structure rotated by 90°, hence the term "pseudorotation". The minimum energy pathway (MEP) was calculated using the nudged elastic band (NEB) method³⁰. The MEP represents the set of most likely trajectories that atoms will follow when physically transitioning between these states, and NEB

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calculations discretize the distortion pathway into a sequence of "images". The highest energy point on the MEP is known as the transition state and corresponds to $\lambda = 0$ in Figure 1-2. The energy of the transition state corresponds to the activation energy.





The symmetric energy profile in **a** is guaranteed by the 4*mm* symmetry. The PF1 bond length function plotted in **b** is also guaranteed to be symmetric and PF2 and PF3 are required to be mirror images.

The MEP of the PF₅ pseudorotation was determined to have $4*mm^*$ symmetry (see Section 1.2.2). A polynomial fit to the energy profile, ΔE , of the

MEP, shown in Figure 1-2a, is symmetric, *i.e.* it is invariant under $/ \rightarrow -/$. This is required by the distortion symmetry, 4^*mm^* . Because 1* commutes with all spatial operations, the action of any starred symmetry operation on a coefficient of the $P(\lambda)$ expansion can be determined, where P is any property of the system. Specifically, the energy, $P = \Delta E$ in Figure 1-2 is a scalar property and is invariant under rotation. By applying tensor transformation rules, we find that $4^*\Delta E(\lambda)$ $=\Delta E(-\lambda)$. However, since 4^* is a symmetry operation, Neumann's principle^{31,32} states that $4^*\Delta E(\lambda) = \Delta E(\lambda)$. Equating the two, one obtains $\Delta E(\lambda) = \Delta E(-\lambda)$.

In other words, $\Delta E(\lambda)$ is a symmetric function of λ , which is consistent with the even order polynomial fit in Figure 1-2. The three bond lengths, PF1, PF2, and PF3, also follow the requirements of the 4*mm* symmetry as shown in Figure 1-2. For example, 4*(PF1(λ))=PF1($-\lambda$), 4*(PF2(λ))=PF3($-\lambda$), and 4*(PF3(λ))=PF2($-\lambda$). Since 4* is a symmetry of the distortion, by Neumann's principle, PF1(λ)=PF1($-\lambda$), PF2(λ))=PF3($-\lambda$), and PF3(λ))=PF2($-\lambda$). This is consistent with the results of the NEB calculation shown in Figure 1-2b.

1.1.2 The symmetry of oxygen diffusion on graphene

Distortion symmetry can provide a systematic way of exploring MEPs between two states. This is demonstrated in the NEB calculation of activation energy for an oxygen atom diffusing across a C₆ ring on the surface of graphene (Figure 1-3). Linear interpolation from the oxygen on the right (λ =-1), to the oxygen on the left (λ =+1) creates a path with *m***m*2* symmetry, with a high

activation energy barrier. Relaxing this path using NEB cannot and does not change the symmetry, because NEB iterations must conserve distortion symmetry (see Section 1.3.2). Instead, with the knowledge of the m^*m2^* symmetry of this path, we can now systematically explore lower symmetry perturbations, such as 2^{*}, m^{*}, m, and 1, as shown in Figure 1-3a,b. Figure 1-3e shows that the initial path with only trivial symmetry (i.e. point group 1) relaxes to a much lower energy path with m^* symmetry. Because NEB can only raise the symmetry of the path, not lower it, the 2^{*} path cannot achieve the same results and has approximately the same energy as the original relaxed m^*m2^* path. Essentially the same path as our m^*m^{2*} path was studied by Dai et al.³³ and they reported a high-energy transition state with a barrier of 1.75 eV (Dai et al. also report a lower energy transition state, apparently similar to our 0.66 eV state, but with 0.81 eV and an energy profile that erroneously violates the m^* symmetry that their path is required to have). Thus, considering distortion symmetry in this example has resulted in lowering the calculated activation energy by a factor of ~5X and in properly symmetrizing the energy profile.



Figure 1-3. The consequences of distortion symmetry and balanced forces for NEB calculations.

Superimposed images along oxygen diffusion paths on graphene after NEB. Starting from a m^*m^{2*} path that goes directly across a C₆ ring, perturbations were added with 2* symmetry in **a** and trivial symmetry in **b**. These perturbations are exaggerated; the maximum displacement of oxygen along the path was 0.1 Å in **a** and about 0.18 Å in **b**. **c** and **d** show the final paths after NEB relaxation starting from the perturbed paths of **a** and **b** respectively. **e** shows the calculated energies of the images and the interpolation provided by Quantum Espresso's NEB module³⁴.

1.1.3 The symmetry of a β -BaB₂O₄ distortion

Next we consider the application of distortion groups to solid-state crystals and the implications for macroscopic property tensors using beta barium borate, β -BaB₂O₄, a widely used nonlinear optical crystal, as an example. Using a parent structure (λ =0) with R3c symmetry³⁵, a distortion with R3c variants at λ =-1 and λ =+1 is constructed, where the displacements scale linearly with λ . This distortion has $R\bar{3}^*c$ symmetry. The calculated energy profile, $\Delta E(\lambda)$, is shown in Figure 1-4a and is symmetric with respect to λ . This is a consequence of the starred symmetry operations, just as with the PF_5 example. In Figure 1-4b, the sequence of intermediate structures along the distortion pathway is depicted by superimposing the structures with colors varying from orange to magenta to cyan as λ varies from -1 to 0 to +1. From the blurred pattern, we can see that this distortion is mostly the nearly rigid rotation of the B_3O_6 rings. For β -BaB₂O₄ and distortion group $R\overline{3}^*c$ (No. 4306 in the complete double antisymmetry space group (DASG) listing^{36,37}), the B_3O_6 rings are on the 12c site. From referring to the listing, we can see this means that there are rings located at $\{0,0,z\}, \{0,0,-z+\frac{1}{2}\},$ $\{0,0,-z\}$, and $\{0,0,z+\frac{1}{2}\}$ with rotation vectors of $[0,0,\omega_z]$, $[0,0,\omega_z]$, $[0,0,-\omega_z]$, and $[0,0,-\omega_z]$ ω_z] respectively. This tells us that the $R\bar{3}^*c$ symmetry requires that the rotation (ω) of the rings is only along the z-axis and alternates every two rings along the column, i.e. clockwise, clockwise, counterclockwise, counterclockwise, etc. The symmetry listing also tells us that the displacement of the rings is only along the z axis and all the rings displace in the same direction with the same magnitude.



Figure 1-4. The application of distortion symmetry to a distortion of β -BaB₂O₄.

The energy profile in Figure 1-4a is symmetric due to the starred symmetry. The structures at λ =-1, 0, and +1 are depicted in orange, magenta, and cyan respectively. Figure 1-4b shows the superimposed images of β -BaB₂O₄ along the distortion pathway from λ =-1 to +1; their color varies from orange to cyan as λ varies from -1 to +1. Figure 1-4c shows the SHG coefficients along this pathway calculated by Cammarata & Rondinelli³⁵ and a polynomial fit using only the coefficients that are consistent with $\overline{3}^*m$ symmetry.

In Figure 1-4c, the calculated values from Cammarata & Rondinelli³⁵ for optical second harmonic generation (SHG) coefficients for this crystal are plotted along the distortion pathway. The SHG interaction, $P_i^{2\omega} = d_{ijk}E_j^{\omega}E_k^{\omega}$, creates a nonlinear polarization *P* at a frequency of 2ω by combining two photons with electric fields *E* at frequency ω . The macroscopic point group of the β -BaB₂O₄ distortion described above is $\bar{3}^*m$. Assuming that the d_{ijk} coefficients are analytic functions with respect to λ , we can write them as a Taylor series: $d_{ijk}(\lambda) = A_{ijk} + B_{ijk}\lambda + C_{ijk}\lambda^2 + D_{ijk}\lambda^3 + \cdots$. $\bar{1}^*$, an element of $\bar{3}^*m$, combined with Neumann's principle, requires that $d_{ijk}(\lambda) = -d_{ijk}(-\lambda)$. Thus it is determined that $d_{ijk}(\lambda)$ should be odd with respect to λ and the even coefficients (A, C, etc.) should be exactly zero. It also means that $d_{ijk}(0)=0$. The points marked by open circles at $\lambda=1.0$ and $\lambda=2.0$ are from previously reported calculations³⁵. The curves are the result of solving for $d_{ijk}(\lambda)=B_{ijk}\lambda+D_{ijk}\lambda^3$ that goes through these points. The above example demonstrates how applying distortion symmetry predicts the form of the tensors that describe the change in any property as a function of the

distortion parameter λ . It can significantly reduce the number of tensor coefficients that can be non-zero.

1.1.4 Other examples



Figure 1-5. Four different distortions in crystals and their distortion symmetry groups.

a shows a distortion pathway between two domain variants of alpha quartz, passing through beta quartz at λ =0. **b** shows a distortion of PbTiO₃ created by linearly interpolation between opposite polarization states. **c** shows a distortion of YMnO₃ between opposite domain variants. **d** shows a B_{1u} normal mode of YBa₂Cu₃O_{6.5}.

The ubiquitousness of distortion symmetry is further illustrated in Figure 1-5

with four final examples. Each panel depicts the structures from λ =-1 to λ =+1

superimposed so that the movement of the atoms appears in the form of a blur.

A common piezoelectric crystal quartz (SiO_2) is depicted in Figure 1-5a, where a distortion from one domain of alpha quartz (at λ =-1) through beta quartz (at λ =0) to another domain of alpha (at λ =+1) exhibits the macroscopic distortion symmetry of 6*22*. Figure 1-11 shows how there is equivalent pathway in lefthanded quartz with P62*22* symmetry, as well as the symmetries of paths between left and right handed quartz. A prototypical proper ferroelectric, PbTiO₃ is depicted in Figure 1-5b, where the distortion pathway runs between opposite polarization states and has P4/m*mm symmetry. An improper ferroelectric antiferromagnet, YMnO₃, distorting from one ferroelectric domain, α^+ at λ =-1 to the opposite domain α^- at λ =+1 exhibits a distortion symmetry of P63/m*cm. Including antiferromagnetism and weak canted ferromagnetism³⁸, we can consider two cases: either spins reverse or spins are invariant through α^+ $\rightarrow \alpha^{-}$. The former has P6₃'/m^{*} symmetry and the latter has P6₃'/m^{*} symmetry. Note that these double antisymmetry space groups involve two independent antisymmetries, 1* and 1'. A complete listing of the 17,803 double antisymmetry space groups has recently been made available^{36,37}. These kinds of distortion pathways should exist in most ferroelectrics and multiferroics. The 670 cm⁻¹ B_{1u} mode of a superconductor, YBa₂Cu₃O_{6.5}, is shown in Figure 1-5d²⁰. This mode has a distortion symmetry of *Pm*mm*, and has recently been shown to couple with A_g modes to create a transient structure that was reported to exhibit room temperature coherent interlayer transport on picosecond time scales reminiscent of superconductivity^{21,22}. Including the coupling between this B_{1u} mode and the A_g modes retains the same distortion symmetry.

An obvious area for immediate benefits would be in implementing distortion symmetry in the NEB codes. Current computational codes such as Quantum Espresso³⁴, VASP³⁹, VTST Tools^{40,41}, Material Studio's DMol³ module³⁰, and AMBER⁴², do not account for distortion symmetry and, consequently, are inefficient due to redundant calculations and sometimes inaccurate due to unsymmetrized numerical errors. Based on a brief literature survey, diffusion studies appear to account for the majority of NEB calculations. Incorporating distortion symmetry into NEB codes would dramatically improve both the speed and quality of the computation of activation barriers for diffusion pathways. Memory usage could potentially be reduced by a factor of two, due to only requiring half as many asymmetric images. The central processing unit (CPU) time required for NEB convergence depends on how long each NEB iteration takes and the number of iterations required to reach convergence. Assuming both of these factors are proportional to the number of asymmetric images, overall CPU time could be reduced by a factor of four. It may not actually be quite this large in practice, but it should still be significant due to eliminating up to half of the asymmetric images.

1.2 Methods

1.2.1 The decomposition seen in Figure 1-1 and the basis of Figure 1-6

The decomposition applied to the simple distortion seen in Figure 1-1 was performed by selecting a basis for translation, rotation, scaling, and deformation

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components. Figure 1-6 shows an example of such a basis and, in this case, it is also symmetry-adapted. After the basis is selected, the displacement vectors are projected onto it and each component can be isolated as shown in Figure 1-1. This and other notions of decomposition into rotational and non-rotational components were explored in our attempts to formalize the concepts of rotation-reversal symmetry as will be discussed further in Chapter 4.

1.2.2 PF₅ Pseudorotation Nudged Elastic Band (NEB) Calculations

The PF₅ pseudorotation minimum energy pathway was computed using Materials Studio 6.0's DMol³ module³⁰. The approximate structure was input using Materials Studio's tools and then geometrically optimized using the DMol³ module. This structure was taken as the λ =-1 variant and was copied and rotated 90° around the high symmetry axis to make the λ =+1 variant. Then the Reaction Preview tool was used to match the atoms of the structures and generate an initial guess path. This guess was used as input for the DMol³ Transition State Search tool whose output was then run in the Transition State Conformation Tool which uses the NEB method to find a minimum energy pathway. The output from NEB was symmetrized to remove the small asymmetric numerical errors and used to construct the plots in Figure 1-2.

1.2.3 Oxygen diffusion on graphene NEB Calculations

The geometrically optimized structure was from an example calculation used at the QE2014 workshop held at Penn State. The λ =-1 structure consists of a 3x3 supercell of graphene with an oxygen atom bonded to the surface, as part of an epoxy functional group. This was mirrored to create the λ =+1 structure. These structures were used as the first and final images in the input for Quantum Espresso's NEB module (neb.x)³⁴. Seven images were used. These are linearly interpolated from the first and final images. This initial guess path, discretized into a chain of seven images, relaxed into the path seen in Figure 1-3a and b with *m*m*2* symmetry.

Next, two new paths were created from the m^*m2^* path using small symmetry breaking perturbations on the oxygen trajectory parallel to the graphene sheet. The first was a sinusoidal perturbation with an amplitude of 0.1 Å resulting in a path with 2* symmetry. The second was a perturbation of $(-\lambda^5-5\lambda^4-6\lambda^3+2\lambda^2+7\lambda+3)/32$ Å resulting in a path with only trivial symmetry (*i.e.* point group 1). These two new paths were then relaxed using QE's NEB module again to get the paths shown in Figure 1-3c and Figure 1-3d.

The reason that starred symmetry operations affect the results of NEB calculations in this way is because NEB commutes with 1* in the same way that conventional symmetry operations commute with physical laws. Clearly, NEB(X) gives the same result as A⁻¹NEB(AX) where X is the initial guess path and A is an ordinary symmetry operation, such as a rotation or a mirror. Similarly, NEB(X) gives the same result as 1*-1NEB(1*X) and, since 1*-1=1*, 1*NEB(1*X). This is no

different from the idea that physical laws should not depend on what basis one chooses for their coordinate system. If A^* is a symmetry of the initial guess path, *i.e.* $X = A^*X$, then, by substitution, NEB(X) = $A^*NEB(X)$. Thus the commutativity of A^* with NEB guarantees that $X = A^*X$ implies NEB(X) = $A^*NEB(X)$, *i.e.* that a symmetry of the initial guess will also be a symmetry of the results. In practice, however, $A^{-1}NEB(AX)$ is not exactly equal to NEB(X) because the NEB implementation will have small symmetry breaking numerical errors.

1.2.4 β -BaB₂O₄ (BBO) Calculations

The β -BaB₂O₄ distortion shown in Figure 1-4 was created using the Materials Studio's Reaction Preview tool by matching atoms of a β -BaB₂O₄ variant with its inverted variant. The result is a path that goes through an $R\bar{3}c$ intermediate, as shown in Figure 1-4a and Figure 1-4b. The energy along this path, as plotted in Figure 1-4a, was computed using Materials Studio's CASTEP module and symmetrized to remove small asymmetric numerical errors. Similar methods were applied to make the energy plot for the quartz example in Figure 1-6.

This β -BaB₂O₄ distortion path is similar, but not identical, to the linear path implied by Cammarata & Rondinelli³⁵ where the displacements from the hypothetical $R\overline{3}c$ parent structure are scaled by a factor. In particular, the path from the Reaction Preview tool has rigid or near rigid rotation of the B₃O₆ rings whereas linearly scaling the displacements creates a path that diverges from rigid rotation as rotation angle increases. Nonetheless, as the two paths are still very similar and have the same distortion symmetry, the results of Cammarata & Rondinelli³⁵ to create Figure 1-6.

1.2.5 Determining distortion symmetry group

Let $S(\lambda)$ denote the structure at λ . Let $G(\lambda)$ denote the conventional symmetry group of $S(\lambda)$. If there is exists $A \in G(\lambda = 0)$ such that $AS(\lambda) = S(-\lambda)$ for all $-1 \le \lambda \le +1$, then the symmetry of the distortion is $H \cup 1^*AH$ where H = $\bigcap_{-1 \le \lambda \le +1} G(\lambda)$. Otherwise, H is the symmetry of the distortion. In other words, find the conventional symmetry group of all the images in a pathway (λ from -1 to +1); the intersection of these groups is the group H. Now find an element A in the conventional symmetry group of the structure at $\lambda = 0$ that can transform a structure at λ to a structure at $-\lambda$. The distortion group of the pathway is then $H \cup A^*H$.

1.3 Supplemental Discussions

1.3.1 Connection between distortion symmetry and representation analysis

The connection between distortion symmetry and representation analysis is further established with the example of atomic displacements of a water molecule, H₂O, with conventional symmetry mm2 (C_{2v}) as depicted in Figure 1-6a. Using the irreducible representations of mm2, we can construct a symmetry-adapted basis for the atomic displacements of H₂O. The chosen basis is depicted in Figure 1-6a. Each of the basis modes correspond to a distortion path that is constructed by linearly scaling the displacements by λ , as was depicted in Figure 1-1c. The irrep carried by the span of each mode in our basis is labeled along with the symmetry of the corresponding distortion. The A1 distortions have mm2 symmetry. The A_2 , B_1 , and B_2 distortions have m^*m^*2 , m*m2*, and mm*2* symmetries respectively. The properties of mm2 allow for this simple correspondence between irreps and distortion groups. In general though, such correspondences can be more complex. For example, the ammonia molecule, NH₃, has 3*m* symmetry. 3*m* has a 2-dimensional irrep, denoted E. This irrep is carried by the linear span of v_1 and v_2 shown in Figure 1-6b. If we construct distortions by linearly scaling v_1 and v_2 by λ , then the resulting distortions have symmetry m and m^* respectively. Thus, knowing the irreducible components of a set of displacements is not equivalent to knowing the symmetry of the corresponding distortion. The symmetry of distortions constructed from linear combinations of v_1 and v_2 is shown in Figure 1-6c. While most of this space (orange region) does have the kernel symmetry of 1, one can see specific linear combinations of v_1 and v_2 (black lines) which give rise to m and m^{*} symmetries. Some of the complexities of representation analysis can be avoided by using distortion symmetry. For many problems, distortion symmetry offers a simple and elegant alternative to traditional representation analysis.


Figure 1-6. A comparison of representation analysis and distortion symmetry for simple molecules.

A symmetry-adapted basis is given in **a** for the atomic displacements of a water molecule. Displacement vectors v_1 and v_2 for NH₃ and their distortion symmetry in **b**. The symmetry of linear combinations of v_1 and v_2 in **c**.

An improper ferroelectric antiferromagnet, YMnO₃, distorting from one ferroelectric domain, a^+ at λ =-1 to the opposite domain a^- at λ =+1 exhibits a distortion symmetry of P6₃/m^{*}cm (Figure 1-5c). This is also effectively the distortion implied by Fennie and Rabe⁴³ in studying the P6₃/mmc parent structure. It is also an interesting case in terms of the relationship between distortion symmetry and representation analysis. Fennie and Rabe identify an unstable K_3 phonon mode of the $P6_3/mmc$ parent structure as driving the improper ferroelectric transition. K_3 is a 2D irrep and thus corresponds to two order parameters. Depending on order parameter direction, a perturbation that transforms as K₃ could result in $P6_3cm$, P3c1, or P3c1 type symmetry. $P6_3cm$ and $P\bar{3}c1$ correspond to 1D subspaces of K₃ and their transformation properties should require that the corresponding distortions have $P6_3/m^*cm$ and $P6_3^*/m^*cm^*$ symmetry respectively. P3c1 is the kernel, the lowest possible symmetry achievable with a perturbation that transforms as K_3 ; it is the symmetry of a general point in the 2D order parameter space of K₃. Distortions corresponding to these points should have $P\overline{6}^*c2^*$ symmetry. In the YMnO₃ case, the order parameter direction corresponds to $P6_3/m^*cm$ and the coupled modes should not change this. Note the considerable complexity of describing the symmetry of this distortion with representation analysis (i.e. the last few sentences) versus comparative simplicity of the distortion symmetry classification (i.e. $P6_3/m^*cm$). This is an advantage of distortion symmetry over conventional representation analysis. Also note that giving the primary irrep of a distortion is not equivalent to giving a distortion group, just as is the case with magnetic symmetry²⁸, because

K₃ actually corresponds to three different types of distortion symmetry: $P6_3/m^*cm$, $P6_3^*/m^*cm^*$, and $P\overline{6}^*c2^*$.

1.3.2 Additional analysis of Figure 1-3: The consequences of distortion symmetry and balanced forces for NEB calculations

This section contains additional analysis about the oxygen diffusion on a graphene surface seen in Figure 1-3. The initial path created by linearly interpolating between $\lambda = -1$ and $\lambda = +1$ has m^*m^{2*} , or more specifically $m_x^*m_y^2z_z^*$ symmetry where the subscripts represent the axis associated with the operation: m_x^* is a starred mirror whose normal is along x, m_y is a mirror whose normal is along y, and $2z^*$ is a starred two-fold axis along z (see compass on lower left in Figure 1-7). Applying Neumann's principle to the force on the oxygen atom gives the following results:

- $m_y F_y(\lambda) = -F_y(\lambda) = F_y(\lambda)$, hence $F_y(\lambda) = 0$ (see **red** in Figure 1-7)
- $m_x^* F_x(\lambda) = -F_x(-\lambda) = F_x(\lambda)$, hence $F_x(\lambda)$ is an odd function of λ (see **blue**)
- $2z^* F_z(\lambda) = F_z(-\lambda) = F_z(\lambda)$, hence $F_z(\lambda)$ is an even function of λ (see **green**)

Clearly, the forces on both the initial and converged path are consistent with these in Figure 1-7. The forces of one iteration are used to update the positions for the next iteration, thus guaranteeing that the $m_x*m_y2_z*$ symmetry cannot be broken in any subsequent iteration.



Figure 1-7. Electrostatic forces on oxygen for the m^*m^{2*} path.



In Figure 1-8, we deliberately break the $m_x*m_y2_z*$ symmetry with a sinusoidal perturbation (the green curve is exaggerated; the maximum displacement was 0.1 Angstrom). Note that the forces on the initial path are similar to the unperturbed case, because the perturbation is small, but slightly break the previous symmetry. The perturbation is such that the path retains 2_z* symmetry. Again applying Neumann's principle to the force on the oxygen atom gives the following results:

- $2_z * F_y(\lambda) = -F_y(-\lambda) = F_y(\lambda)$, hence $F_y(\lambda)$ is an odd function of λ (see red)
- $2z^* F_x(\lambda) = -F_x(-\lambda) = F_x(\lambda)$, hence $F_x(\lambda)$ is an odd function of λ (see **blue**)
- $2_z * F_z(\lambda) = F_z(-\lambda) = F_z(\lambda)$, hence $F_z(\lambda)$ is an even function of λ (see **green**)

Again, this is consistent with the forces on both the initial and converged path in Figure 1-8. The 2_z^* symmetry in the initial guess prevents NEB iterations from finding a significantly lower transition state (TS).



Figure 1-8. Electrostatic forces on oxygen for the 2* perturbed path.

Left: perturbation from m^*m2^* path (green curve) with 2^* symmetry diagram overlaid. Right: x, y, and z component of the force on oxygen for the initial path (dashed) and the final converged path (solid with axis filling).

In Figure 1-9, we deliberately break the m_x*m_y2z* symmetry to trivial symmetry (the green curve is exaggerated; the maximum displacement was 0.18 Angstrom). Note that the forces on the initial path are similar to the unperturbed case, because the perturbation is small, but slightly break all previous symmetry. NEB iterations drive the path to the much lower energy m* path seen in Figure 1-3d of the main text.







Figure 1-10 shows two other ways of breaking m^*m^{2*} symmetry. We expect that NEB would drive the m^* initial path (left side of Figure 1-10) to the same low energy m^* path seen in Figure 1-3d of the main text. The *m* initial path (right side of Figure 1-10) should not be able to converge to the low energy m^* path because *m* is not a subgroup of m^* and NEB iterations must conserve distortion symmetry.



Figure 1-10. Possible m^* and m perturbations.

Left: perturbation from m^*m2^* path (green curve) to an m^* symmetry path. Right: perturbation from m^*m2^* path (green arrows indicating carbon displacements) to an *m* symmetry path.



1.3.3 Example of 1* switching handedness for a distortion of quartz



a Some distortion pathways and their distortion symmetry between left and right handed variants of α -quartz and β -quartz. **b** The energy of the P64*22* distortion as a function of λ .

Figure 1-11 shows the example of quartz, a common crystal that is found in left- and right- handed configurations, and is commonly used in watches and clocks as a crystal oscillator by using its piezoelectric effect. Trigonal α -quartz transforms into hexagonal β-quartz at 573°C, into hexagonal β-tridymite at 870°C and to cubic β -cristobalite at 1470°C. If β -quartz is considered a parent, the distortion to α -quartz has P6₂*22* symmetry for left-handed quartz and P6₄*22* symmetry for right-handed quartz (this is the distortion depicted in Fig. 6a of the main text). Note that $\lambda = +1$ and $\lambda = -1$ are different variants of α -quartz with β guartz structurally intermediate between the two. In this instance, 1* does not reverse the handedness of the structures. However, if an appropriate parent is chosen, one can also transform between left- and right-handed α -quartz, as well as between left- and right- handed β -quartz. For α -quartz, our path has Am*m*2 symmetry. For β -quartz, our path has Cm*m*m* symmetry. This demonstrates a potentially surprising property of 1*, namely, that it can, for carefully selected paths, 1* reverse the handedness of a crystal. However, our $\lambda = 0$ structure clear not physically reasonably for either the Am*m*2 symmetry path or the Cm*m*m* symmetry path so it is very unlikely that it could be activated experimentally in practice. Other choices of paths are possible with the same or different distortion symmetries so there may be other paths with more reasonable transition states.

More generally, one can find distortion groups describing transformation between any two enantiomorphic structures (related by mirror) by choosing an appropriate parent that is intermediate between the two. Multiple such parents

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are possible, in principle. These ideas are also applicable to liquid crystals which can switch between left- and right- handed enantiomorphs under an electric field, a property that is utilized in computer displays. Figure 1-11b shows that, as with the examples given in the main text, the energy of the P64*22* distortion is symmetric with respect to λ due to the starred symmetry.

1.3.4 Examples of published studies that could have benefited from the application of distortion groups.

Reference	Figure(s) with starred symmetry consequences	Description and notes
Durinck, J., Legris, A. & Cordier, P. Pressure sensitivity of olivine slip systems: First-principle calculations of generalised stacking faults. Phys. Chem. Miner. 32, 646–654 (2005).	3,4,5,6	Stacking faults in olivine. All figures that should be symmetric due to starred symmetry show some degree of asymmetric error, Fig. 6 in particular. In part, this is due to having an even number of image.
Dai, Y., Ni, S., Li, Z. & Yang, J. Diffusion and desorption of oxygen atoms on graphene. J. physics. Condens. matter. 25, 405301 (2013).	3	Both Fig. 3a and 3b should be symmetric due to starred symmetry. Fig. 3a is a particularly extreme example of asymmetry error. The path taken in Fig. 3b is unstable and is balanced by symmetry as discussed in the main text.

Table 1-1. Examples of published studies that could have benefited from the application of distortion groups.

Zhou, B., Shi, H., Cao, R., Zhang, X. & Jiang, Z. Theoretical study on the initial stage of Magnesium battery based on V2O5 cathode. Phys. Chem. Chem. Phys. 16, 18578– 18585 (2014).	3	Diffusion of Li and Mg in V ₂ O ₅ . The energy profiles show significant asymmetry error.
Ma, W. Y., Zhou, B., Wang, J. F., Zhang, X. D. & Jiang, Z. Y. Effect of oxygen vacancy on Li-ion diffusion in a V2O5 cathode: a first- principles study. J. Phys. D. Appl. Phys. 46, 105306 (2013).	4a,c	Calculated energy for three different diffusion pathways for Li in V ₂ O ₅ using NEB. Paths A and C have starred symmetry and thus figures 4a and 4c are symmetric. Path B does not have starred symmetry and thus figure 4b is asymmetric.
Morgan, B. J. & Watson, G. W. GGA+U description of lithium intercalation into anatase TiO2. Phys. Rev. B - Condens. Matter Mater. Phys. 82, 1–11 (2010).	8b,c	Calculated energy of Li diffusion pathway in TiO ₂ using NEB. The pathways for Fig 8b and 8c have starred symmetry and thus the energy plot is symmetric. Fig 9 depicts this pathway.
Yang, J., Hu, W. & Tang, J. Surface self-diffusion behavior of individual tungsten adatoms on rhombohedral clusters. J. Phys. Condens. Matter 23, 395004 (2011).	3	NEB study of diffusion of tungsten adatom on tungsten cluster surface. Figure 3 shows symmetric energy due to starred symmetry.
Tsuru, T. et al. Solution softening in magnesium alloys: the effect of solid solutions on the dislocation core structure and nonbasal slip. J. Phys. Condens. Matter 25, 022202 (2013).	1c and 3a-d	Energy versus slip in magnesium alloys. Energy is symmetric for prismatic slip in Figure 1c due to starred symmetry. Symmetric energy in Figure 3a and 3b due to starred symmetry. The restoring force is antisymmetric in Figure 3c and 3d due to starred symmetry.

Mulroue, J., Uberuaga, B. P. & Duffy, D. M. Charge localization on the hexa- interstitial cluster in MgO. J Phys Condens Matter 25, 65502 (2013).	6	Diffusion path of MgO/O ₃ cluster in MgO. Figure 6 is symmetric due to starred symmetry, but has small asymmetric errors.
Gröger, R. & Vitek, V. Constrained nudged elastic band calculation of the Peierls barrier with atomic relaxations. Model. Simul. Mater. Sci. Eng. 20, 035019 (2012).	2,3,4, and 5b	Constrained nudged elastic band calculation of the Peierls barrier with atomic relaxations. There are small but apparent deviations from symmetry (numerical errors). Fig. 5b shows only half of the pathway, due to symmetry.
Schusteritsch, G. & Kaxiras, E. Sulfur-induced embrittlement of nickel: a first-principles study. Model. Simul. Mater. Sci. Eng. 20, 065007 (2012).	7	Stacking faults in Ni. Figure 7b (Theta=0.0) and 7c(Theta=0.0) are antisymmetric due to symmetry.
Wu, M. H., Liu, X. H., Gu, J. F. & Jin, Z. H. DFT study of nitrogen – vacancy complexions in (fcc) Fe. Model. Simul. Mater. Sci. Eng. 22, 055004 (2014).	4a	N diffusion in fcc Fe. Fig. 4a is symmetric due to starred symmetry.
Lawrence, B., Sinclair, C. W. & Perez, M. Carbon diffusion in supersaturated ferrite: a comparison of mean-field and atomistic predictions. Model. Simul. Mater. Sci. Eng. 22, 065003 (2014).	3	Carbon diffusion in supersaturated ferrite. Figure 3 (x _c = 0) is symmetric due to starred symmetry.

Samanta, A. & Weinan, E. Optimization-based string method for finding minimum energy path. Commun. Comput. Phys. 14, 265–275 (2013).	2,3	Ad-atom diffusion on copper surface. Figs. 2 and 3 are symmetric due to starred symmetry.
Zelený, M. et al. Ab initio study of Cu diffusion in α- cristobalite. New J. Phys. 14, (2012).	N/A	Cu diffusion in cristobalite. None of these figures are symmetric due to starred symmetry. Some are nearly symmetric barriers, but not exact. This is an example that shows that apparent symmetry in energy plots is not necessarily due to distortion symmetry (and therefore not exact).
Mulroue, J. & Duffy, D. An ab initio study of the effect of charge localization on oxygen defect formation and migration energies in magnesium oxide. Proc. R. Soc. London. A. Math. Phys. Sci. 467, 2054–2065 (2011). ⁵⁷	2,3	An ab initio study of the effect of charge localization on oxygen defect formation and migration energies in magnesium oxide. Figs. 2 and 3 are symmetric due to starred symmetry.
Tingaud, D., Nardou, F. & Besson, R. Diffusion in complex ordered alloys: Atomic-scale investigation of NiAl3. Phys. Rev. B - Condens. Matter Mater. Phys. 81, 1–8 (2010).	3	Fig. 3 is a comparison of NEB and constrained atom (CA) methods. Both show small asymmetry errors. Diffusion in NiAl3. Fig. 3 is symmetric due to starred symmetry.

Śpiewak, P. & Kurzydłowski, K. J. Formation and migration energies of the vacancy in Si calculated using the HSE06 range- separated hybrid functional. Phys. Rev. B - Condens. Matter Mater. Phys. 88, 1–6 (2013).	3	Vacancy diffusion pathway, CI-NEB. Fig. 3 is symmetric due to starred symmetry.
Kumagai, T. et al. H-atom relay reactions in real space. Nat. Mater. 11, 167– 172 (2011).	4	H-atom relay reactions in real space. Fig. 4 is symmetric due to starred symmetry.
Pizzagalli, L. et al. A new parametrization of the Stillinger-Weber potential for an improved description of defects and plasticity of silicon. J. Phys. Condens. Matter 25, 055801 (2013).	2	Stacking fault energy. Figure 2 is symmetric due to starred symmetry.
Pei, Z. et al. Ab initio and atomistic study of generalized stacking fault energies in Mg and Mg-Y alloys. New J. Phys. 15, 0–19 (2013).	3,4,5	Stacking fault energy in Mg and Mg- Y alloys. Figs. 3, 4, and 5 are symmetric due to starred symmetry.
Ho, G., Ong, M. T., Caspersen, K. J. & Carter, E. a. Energetics and kinetics of vacancy diffusion and aggregation in shocked aluminium via orbital-free density functional theory. Phys. Chem. Chem. Phys. 9, 4951–4966 (2007).	4	Diffusion in aluminum. Figure 4 is symmetric due to starred symmetry.

Panduwinata, D. & Gale, J. D. A first principles investigation of lithium intercalation in TiO2-B. J. Mater. Chem. 19, 3931 (2009).	N/A	Lithium intercalation in TiO2-B. Shows the result of reversed pathways, e.g. Fig. 5.
Berry, S. Correlation of rates of intramolecular tunneling processes, with application to some group V compounds. J. o Chem. Phys. 32, 933–938 (1960).	2	Arrows depicting PF ₅ pseudorotation in Fig. 2. As noted in the main text, these arrows are related by symmetry.
Kushima, A. et al. Interstitialcy diffusion of oxygen in tetragonal La2CoO(4+δ). Phys. Chem. Chem. Phys. 13, 2242–2249 (2011).	2a	Diffusion of oxygen in La ₂ CoO ₄ . Figure 2b shows Initial to Saddle images but not Saddle to Final, implying the intuitive application of symmetry.
Li, W. et al. Li+ ion conductivity and diffusion mechanism in α-Li3N and β- Li3N. Energy Environ. Sci. 3, 1524 (2010).	7	Diffusion in Li ₃ N. Pathways depicted in Fig. 6. Figure 7 is symmetric due to starred symmetry.
Yildirim, H., Greeley, J. P. & Sankaranarayanan, S. K. R. S. The effect of concentration on Li diffusivity and conductivity in rutile TiO2. Phys. Chem. Chem. Phys. 14, 4565 (2012).	3	Li diffusion in TiO2. Figure 3 is symmetric due to starred symmetry.

Ye, XJ., Liu, CS., Jia, R., Zeng, Z. & Zhong, W. How does the boron concentration affect hydrogen storage in lithium decorated zero- and two- dimensional boron-carbon compounds? Phys. Chem. Chem. Phys. 15, 2507–13 (2013).	5	Li diffusion on B_8C_{24} and $B_{24}C_{12}$. The path on B_8C_{24} has starred symmetry and thus the energy plot in Fig. 5c should be symmetric but is not, presumably due to errors. The path on $B_{24}C_{12}$ does not have starred symmetry and the asymmetry of Fig. 5d is consistent with this.
Han, J. W. & Yildiz, B. Mechanism for enhanced oxygen reduction kinetics at the (La,Sr)CoO3– δ /(La,Sr)2CoO 4+ δ hetero-interface. Energy Environ. Sci. 5, 8598 (2012).	3е	O diffusion in La ₂ CoO ₄ . Figure 3e is symmetric due to starred symmetry.
Kuhlman, T. S., Glover, W. J., Mori, T., Møller, K. B. & Martínez, T. J. Between ethylene and polyenes - the non-adiabatic dynamics of cis-dienes. Faraday Discuss. 157, 193 (2012).	5	NEB, molecular transitions. Figure 5 is symmetric due to starred symmetry.

Matsunaga, K. & Toyoura, K. First-principles analysis of oxide-ion conduction mechanism in lanthanum silicate. J. Mater. Chem. 22, 7265 (2012). ⁷²	N/A	Oxygen diffusion in lanthanum silicate. Very interesting pathway from O5-0 to symmetry equivalent O5-0 site depicted in Fig. 9 and Fig. 10. Shows how equivalence of initial and final states (as noted in the captions) does not guarantee symmetry. This can be seen from the labels given along the O5-0 to O5-0 pathways, e.g. in Fig. 10 the pathway goes from O5-0 to O5-s2 to O5-s1 to O5-0. Because O5-s2 and O5-s1 are inequivalent, it is impossible to superimpose this pathway with its reverse and therefore there is no starred symmetry.
Islam, M. S. & Fisher, C. a J. Lithium and sodium battery cathode materials: computational insights into voltage, diffusion and nanostructural properties. Chem. Soc. Rev. 43, 185– 204 (2014).	7	Migration pathway for Li in LiFePO ₄ . Fig.5 also depicts two different kinds of hops that occur in Li _x CoO ₂ , we note that the first (Fig. 5a) has starred symmetry but the other does not.
Cai, Y. et al. Constructing metallic nanoroads on a MoS ₂ monolayer via hydrogenation. Nanoscale 6, 1691–7 (2014).	2	Diffusion of hydrogen atom on MoS ₂ . Figure 2 is symmetric due to starred symmetry.
Murugesan, S. et al. Wide electrochemical window ionic salt for use in electropositive metal electrodeposition and solid state Li-ion batteries. J. Mater. Chem. A 2, 2194 (2014).	N/A	Fig. 6 shows another example of a minimum energy pathway that is not superimposable with its reverse and therefore does not contain starred symmetry.

Gao, Y. et al. Improved electron/Li-ion transport and oxygen stability of Mo- doped Li2MnO3. J. Mater. Chem. A 2, 4811 (2014). ⁷⁶	5a,b	Various migration pathways in Li ₂ MnO ₃ . Path 3 and 4 have starred symmetry, the rest do not.
Wu, J. et al. Tavorite- FeSO4F as a potential cathode material for Mg ion batteries: a first principles calculation. Phys. Chem. Chem. Phys. 16, 22974–22978 (2014).	3,4	Mg diffusion in Mg _{0.5} FeSO ₄ F. L1 and L2 pathways (Fig. 3) both have starred symmetry. Small deviations from this symmetry are apparent in Fig.4, e.g. the 5th and 13th points of Fig. 4a should be at the same height. Presumably this is due to errors in the calculations.
Su, J., Pei, Y. & Wang, X. Ab initio study of graphene- like monolayer molybdenum disulfide as a promising anode material for rechargeable sodium ion batteries. RSC Adv. 4, 43183–43188 (2014).	4	Na migration path on MoS2. Very clear example with superimposed images showing the pathway. Both pathways in Figure 4 have starred symmetry.
Ling, C., Zhang, R. & Mizuno, F. Phase stability and its impact on the electrochemical performance of VOPO4 and LiVOPO4. J. Mater. Chem. A 2, 12330 (2014).	7	Li diffusion in LiVOPO4. Figure 7 is symmetric due to starred symmetry.
Mo, Y., Ong, S. P. & Ceder, G. Insights into Diffusion Mechanisms in P2 Layered Oxide Materials by First- Principles Calculations. Chem. Mater. 26, 5208– 5214 (2014).	3	Na diffusion in NaCoO2. Figure 3 is symmetric due to starred symmetry.

Nishimura, S. et al. Experimental visualization of lithium diffusion in LixFePO4. Nat. Mater. 7, 707–711 (2008). ⁸¹	1c,d and 3	Figure 3 shows the expected diffusion path of Li in LiFePO ₄ . Depicted as continuous motion. Figure 1c,d show two different pathways. Both have clear starred symmetry. Considering only the finite structures depicted, 1c has m*m2* symmetry and 1d has 2*/m symmetry.
Milas, I., Hinnemann, B. & Carter, E. a. Diffusion of Al, O, Pt, Hf, and Y atoms on α -Al2O3(0001): implications for the role of alloying elements in thermal barrier coatings. J. Mater. Chem. 21, 1447 (2011).	3a,d,e	Diffusion on Al ₂ O ₃ surface. Fig. 3a,d, and e are symmetric due to starred symmetry.
Marinica, MC. et al. Interatomic potentials for modelling radiation defects and dislocations in tungsten. J. Phys. Condens. Matter 25, 395502 (2013). ⁸³	2,4,6	Figs. 2, 4, and 6 are symmetric due to starred symmetry.
Chang, H. et al. Single adatom dynamics at monatomic steps of free- standing few-layer reduced graphene. Sci. Rep. 4, 6037 (2014). ⁸⁴	4b	Pathways in Fig. 4a and c have equivalent endpoints, but do not have starred symmetry (the approximate symmetry of the energy in Fig. 4c is not due to starred symmetry). The pathway in Fig. 4b should have starred symmetry but there are clear deviations in the energy (note 2nd and 2nd to last points). The starred symmetry suggests this is an error, maybe due to using an even number of images.
Wang, C. et al. Single Adatom Adsorption and Diffusion on Fe Surfaces. Journal of Modern Physics 02, 1067–1072 (2011). 85	2,3,4	Adatom Diffusion on Fe surfaces. Small asymmetry in Fig 2 due to choosing an even number of points.

Ritzmann, A. M., Pavone, M., Muñoz-García, A. B., Keith, J. a. & Carter, E. a. Ab initio DFT+U analysis of oxygen transport in LaCoO3: the effect of Co3+ magnetic states. J. Mater. Chem. A 2, 8060 (2014).	8	Diffusion in LaCoO3. Fig. 8c is interesting in the context of distortion symmetry because μ A and μ B are related by a starred operation and so they should be opposite with respect to the reaction coordinate and meet in the middle. This is consistent with the figure except they do not meet in the middle. This is either an error or an interesting case of magnetism breaking starred symmetry.
MedeA Transition State Search Datasheet, http://www.materialsdesig n.com/medea/transition- state-search ⁸⁷	2	MedeA Transition State Search Datasheet. Shows an example of applying the MedeA Transition State Search module to the migration of a Pd ₄ cluster on a MgO(001) surface. Figure 2 is symmetric due to starred symmetry.
Sun, Y. et al. Direct atomic- scale confirmation of three-phase storage mechanism in Li4Ti5O12 anodes for room- temperature sodium-ion batteries. Nat. Commun. 4, 1870 (2013).	2d,e (red and blue),f (red and blue)	Diffusion in Li4Ti5O12, Li7Ti5O12, and Na6LiTi5O12. Fig. 2d,e (red and blue),f (red and blue) are symmetric due to starred symmetry.
Khvalkovskiy, A. V. et al. Basic principles of STT- MRAM cell operation in memory arrays. J. Phys. D. Appl. Phys. 46, 074001 (2013).	3	NEB for studying switching of magnetic domains, uniform rotation versus domain wall motion. Data from Dittrich, R. et al. Energy Barriers in Magnetic Random Access Memory Elements. IEEE Trans. Magn. 39, 2839–2841 (2003). Fig. 3 is symmetric due to starred symmetry.

Van Swygenhoven, H., Derlet, P. M. & Frøseth, a G. Stacking fault energies and slip in nanocrystalline metals. Nat. Mater. 3, 399– 403 (2004).	3 (red)	Stacking faults in Ni, Al, and Cu. Fig. 3 (red) is symmetric due to starred symmetry.
Schegoleva, L. N. & Beregovaya, I. V. Manifestation of Complicated Structure of Potential Energy Surfaces in Spectral and Chemical Properties of Haloarene Radical Ions. Fluor. Notes 2, (2013).	10	Pseudo-rotation of 1,2,3- $F_3C_6H_3$. In Figure 10b, starred symmetry has the consequence of making F_2 symmetric and F_1 and F_3 mirror images. This is similar to the PF ₅ pseudorotation and bond lengths example given in the main text of our work.
Park, YU. et al. Tailoring a fluorophosphate as a novel 4 V cathode for lithium-ion batteries. Sci. Rep. 2, 1–7 (2012).	5	Diffusion of Na and Li ions in Na _{1.5} VPO ₅ F _{0.5} and LiNa _{0.5} VPO ₅ F _{0.5} . Fig. 5b and 5d give very clear depictions of the pathways. Fig. 5c and 5e are symmetric due to starred symmetry.
Wang, J., Ewing, R. C. & Becker, U. Average structure and local configuration of excess oxygen in UO2+x. Sci. Rep. 4, 4216 (2014).	1	Fig. 1 is symmetric due to starred symmetry.
Tang, Z. K., Zhang, Y. N., Zhang, D. Y., Lau, W. M. & Liu, L. M. The stability and electronic properties of novel three-dimensional graphene-MoS2 hybrid structure. Sci. Rep. 1–7 (2014).	5	Fig. 5 is symmetric due to starred symmetry.

Shang, S., Hector Jr., L. G., Wang, Y. & Liu, Z. K. Anomalous energy pathway of vacancy migration and self-diffusion in hcp Ti. Phys. Rev. B 83, (2011).	1	Diffusion in Ti. Figure 1 is symmetric due to starred symmetry.
Dathar, G. K. P., Sheppard, D., Stevenson, K. J. & Henkelman, G. Calculations of Li-ion diffusion in olivine phosphates. Chem. Mater. 23, 4032–4037 (2011).	1,2	Li diffusion in olivine phosphates (FePO4 and LiFePO4). All paths with plotted energies are symmetric due to starred symmetry.
Fennie, C. J. & Rabe, K. M. Ferroelectric transition in YMnO3 from first principles. Phys. Rev. B - Condens. Matter Mater. Phys. 72, 1–4 (2005).	2,4	The distortions in this paper come from following the normal modes of a parent structure. Figure 4 is antisymmetric because of the starred symmetry.
Meng, X. et al. Direct visualization of concerted proton tunnelling in a water nanocluster. Nat. Phys. 11, 235–239 (2015).	3a	Figure 3a is symmetric due to starred symmetry.

Chapter 2

Affine and Euclidean normalizers

As will be shown in Chapter 3, normalizers can be applied to evaluate equivalence relations and are therefore of interest for determining the proper affine equivalence classes of double antisymmetry groups. This was the main motivation for the work discussed in this chapter. Although it does not match the chronological order in which the works were performed, I have put this chapter before Chapter 3 because understanding the concepts of this chapter will allow for a deeper comprehension and appreciation of Chapter 3.

Much of the text of this chapter is from "The affine and Euclidean normalizers of the subperiodic groups" by Brian K. VanLeeuwen (myself), Pedro Valentín De Jesús, Daniel B. Litvin, and Venkatraman Gopalan⁹⁷. Because the machine-readable files were generated using algorithms, I think it is possible, or even likely, that they are error-free, unless there was a systematic error that I did not find. I am particularly confident in the affine normalizers as my own results were later independently confirmed by Pedro's. In addition to independently confirming these results, Pedro's work extended the affine normalizer results to the Euclidean normalizers in the way described in this chapter.

Unlike with the computer-generated double antisymmetry space group tables discussed in Chapter 3, the human-readable tables of Euclidean normalizers almost certainly contain some non-systematic errors from typos and other mistakes that come from the more manual way in which they were created. Although Pedro and I have made extensive attempts to minimize these, some no doubt persist.

2.1 Introduction

Informally, a normalizer of a symmetry group can be thought of as the "symmetry of the symmetry pattern", *i.e.* it is the set of transformations that map the symmetry group into itself ⁹⁸. For instance, with the point group 222 which consists of three perpendicular 2-fold rotation axes, a 90° rotation about one of the 2-fold axes would not change the group. Similarly, mirroring across planes perpendicular to one of the 2-fold axes would not change 222. Taking all such operations together, we would find that the group $m\bar{3}m$ is formed. That is to say that $m\bar{3}m$ is the orthogonal normalizer group of 222.

Formally, given a group *S* and a subgroup *G* of *S*, the normalizer group of *G* in *S* is the subgroup of *S* composed of every element *s* in *S* for which $G = sGs^{-1}$; ⁹⁸⁻¹⁰¹. Note that it is not necessary for every element *g* in *G* to satisfy $g = sgs^{-1}$, just *G* as a whole. The normalizer group of *G* in *S* will be denoted $N_S(G)$.

$$N_S(G) = \{ s \in S : G = sGs^{-1} \}$$

The affine normalizer group of a space group is the normalizer group of that space group in the group of affine transformations. Likewise, the Euclidean

ⁱ Note that expressions such as aSa^{-1} where S is a set or a group and a is a transformation should be interpreted as applying asa^{-1} to every element s in S, i.e. $aSa^{-1} = \{asa^{-1}: s \in S\}$.

normalizer group of a space group is the normalizer group of that space group in the group of Euclidean motions. The group of affine transformations will be denoted *A* and the group of Euclidean motions will be denoted *E*. When discussing the rod and layer groups, *A* and *E* will refer specifically to the affine and Euclidean groups of three-dimensional Euclidean space. When discussing the Frieze groups, they will refer to the affine and Euclidean group of twodimensional Euclidean space. To avoid excessive notation, context will distinguish the two and three dimensional cases.

It has been suggested that our listing of the double antisymmetry space group properties and diagrams³⁶ should include the double antisymmetry subperiodic groups similar to Litvin's listing of the 1-, 2-, and 3-dimensional magnetic space and subperiodic groups ¹⁰². This was not possible because the types of double antisymmetry subperiodic groups are not known and the method of evaluating proper affine equivalence discussed by VanLeeuwen et al.³⁷ requires using the affine normalizer groups. Thus, the motivation for the present work, in addition to the value of the normalizer groups themselves, was to make it possible to use this method for the subperiodic antisymmetry groups. Although listing the Euclidean normalizers is not necessary for this purpose, it is a result that may be of some interest to others and we have therefore extended the results to cover this as well.

2.2 Affine normalizers of a translational subgroup

In space groups and subperiodic groups of every dimension, every element is composed of a distance-preserving linear transformation and a translation, such a transformation is called a motion or a Euclidean motion. A motion is a special type of the more general affine transformations. Affine transformations are composed of linear transformations and translations. Affine transformations, unlike motions, do not require the linear part to be distance preserving; hence $E \subset A$. In the present work, affine transformations (and motions as a special case) will be denoted in Seitz notation as $\{a|\vec{t}\}$ where *a* is the linear part and \vec{t} is the translation vector.

The product of affine transformations $\{a_1|\vec{t}_1\}$ and $\{a_2|\vec{t}_2\}$ can be written in Seitz notation as $\{a_1|\vec{t}_1\}\{a_2|\vec{t}_2\} = \{a_1a_2|a_1\vec{t}_2 + \vec{t}_1\}$. The inverse of an affine transformation $\{a|\vec{t}\}$ must therefore be $\{a|\vec{t}\}^{-1} = \{a^{-1}| - a^{-1}\vec{t}\}$. Conjugation can be performed using these Seitz notation expressions.

The conjugation of a pure translation (an affine transformation with identity for the linear part) by an affine transformation is also a pure translation. This is easy to prove by showing that $\{a|\vec{t}\}\{1|\vec{t}'\}\{a^{-1}| - a^{-1}\vec{t}\}\$ simplifies to $\{1|a\vec{t}'\}$. Since the conjugation of a pure translation by an affine transformation is also a pure translation, an element of the affine normalizer of a symmetry group is also an element of the affine normalizer of the translational subgroup (the translational subgroup of a group $G \subset E$ will be denoted Λ and defined by $\Lambda \equiv \{\{1|\vec{t}\} \in G\}\}$, *i.e.* $G = nGn^{-1}$ implies $\Lambda = n\Lambda n^{-1}$ for all for $G \subset E$. Therefore $N_A(G) \subset N_A(\Lambda)$.

Let G be a group of Euclidean motions that transform d-dimensional Euclidean space and Λ be the translational subgroup, if the translation vectors of A span the d-dimensional space and $\Lambda \cong \mathbb{Z}^d$, then it is a d-dimensional space group, if they span a zero-dimensional subspace, it is a d-dimensional point groupⁱⁱ, and if they span a p-dimensional subspace and $\Lambda \cong \mathbb{Z}^p$ where d > p > 0, it is a d-dimensional subperiodic group with p dimensions of periodicity. Figure 2-1 shows how subperiodic groups fill the gap between point and space groups. We will consider a faithful augmented matrix representation of the group G on a basis of p primitive lattice vectors and d-p arbitrary vectors that form an orthogonal basis for the orthogonal complement of the aforementioned pdimensional subspace. This representation of G on this basis and the abstract group itself will not be distinguished. Similarly, the faithful representations of A and E on this basis will not be distinguished from A and E. This representation of G was achieved by a basis transformation from the standard augmented matrix representation in the standard setting using the appropriate centering matrix. The standard augmented matrices we used were downloaded from the Bilbao Crystallographic Server ^{103–105}.

ⁱⁱ More precisely, it is a subgroup of *E* that is naturally isomorphic to a point group.

		<u>Total dimensionality</u>		
_		1	2	3
<u>Periodic</u> <u>dimensions</u>	0	1D Point 2	2D Point 10	3D Point 32
	1	Line 2	Frieze 7	Rod 75
	2		Wallpaper 17	Layer 80
	3			Space 230

Figure 2-1. Number of types of crystallographic symmetry groups across different values of *d* and *p*.

Since $N_A(G) \subset N_A(\Lambda)$, to solve for $N_A(G)$ we will start by deriving the form of all elements of $N_A(\Lambda)$. On this generalized primitive basis, the augmented matrix of a general affine transformation would be represented by a d-by-d invertible matrix of real numbers for the linear part and d real number components for the translation vector. This can be represented as a block matrix $\begin{cases} n & r_{\parallel} \\ c & r_{\perp} \\ \vec{x}_{\perp} \end{cases}$ where n is a *p*-by-*p* submatrix, r_{\parallel} is a *p*-by-(d-p) submatrix, r_{\perp} is (d-p)-by-(d-p)submatrix, \vec{x}_{\parallel} is a *p*-by-1 submatrix (i.e. a p-dimensional "column vector") and \vec{x}_{\perp} is a (d-p)-by-1 submatrix (i.e. a (d-p)-dimensional "column vector"). If this affine transformation is an element of $N_A(\Lambda)$, it should map elements of Λ into elements of Λ . On this basis, elements of Λ are $\{1 | \substack{\vec{l} \\ 0}\}$ where 1 is a d-by-d identity matrix, \vec{t} is a *p*-by-1 submatrix of integers and 0 is a (d-p)-by-1 zero submatrix. Conjugation of $\{1 | \substack{0 \\ 0}\}$ by $\{ \substack{n \\ c} \ r_{\perp} \mid \stackrel{\vec{x}_{\parallel}}{\vec{x}_{\perp}} \}$ yields $\{1 | \substack{n\vec{t} \\ c\vec{t}}\}$. For $\{1 | \substack{n\vec{t} \\ c\vec{t}}\}$ to be an element of Λ , the components of $n\vec{t}$ must be integers and $c\vec{t} = \vec{0}$. Thus for $\{ \substack{n \\ c} \ r_{\perp} \mid \stackrel{\vec{x}_{\parallel}}{\vec{x}_{\perp}} \}$ to be an element of $N_A(\Lambda)$, c must be the zero matrix and n must be a matrix of integers. Furthermore, $|n| = \pm 1$ because the volume of the subperiodic unit cell must be conserved. Given that c must be the zero matrix, we can also find that, in order to guarantee invertibility, $|r_{\perp}|$ must be non-zero, because $| \substack{n \\ 0} \ r_{\perp} \ | = |n| |r_{\perp}|$. Thus, the elements of $N_A(\Lambda)$ are simply the augmented matrices with the following form:

$$\begin{cases} n & r_{\parallel} \\ 0 & r_{\perp} \end{vmatrix} | \vec{x} \Big\}$$

where *n* is a *p*-by-*p* submatrix of integers with $|n| = \pm 1$, r_{\parallel} is a *p*-by-(d - p)submatrix of real numbers, r_{\perp} is (d - p)-by-(d - p) submatrix of real numbers with $|r_{\perp}| \neq 0$, and \vec{x} is the translational vector whose coordinates are real numbers.

For the Frieze groups, which are two dimensional subperiodic groups with one periodic dimension (d = 2, p = 1):

$$N_A(\Lambda) = \left\{ \begin{cases} \pm 1 & r_{12} \\ 0 & r_{22} \end{cases} \mid \begin{array}{c} x_1 \\ x_2 \end{cases} : r_{22} \neq 0 \land r_{ij}, x_i \in \mathbb{R} \end{cases} \right\}$$

For the rod groups, which are three dimensional subperiodic groups with one periodic dimension (d = 3, p = 1) with the translations along [100] rather than the rod group convention of [001] :

$$N_A(\Lambda) = \left\{ \begin{cases} \pm 1 & r_{12} & r_{13} & x_1 \\ 0 & r_{22} & r_{23} & | & x_2 \\ 0 & r_{32} & r_{33} & x_3 \end{cases} : \begin{vmatrix} r_{22} & r_{23} \\ r_{32} & r_{33} \end{vmatrix} \neq 0 \land r_{ij}, x_i \in \mathbb{R} \right\}$$

Rearranged for translations along [001]:

$$N_A(\Lambda) = \left\{ \begin{cases} r_{11} & r_{12} & 0 & x_1 \\ r_{21} & r_{22} & 0 & | & x_2 \\ r_{31} & r_{32} & \pm 1 & x_3 \end{cases} : \begin{vmatrix} r_{11} & r_{12} \\ r_{21} & r_{22} \end{vmatrix} \neq 0 \land r_{ij}, x_i \in \mathbb{R} \right\}$$

For the layer groups, which are three dimensional subperiodic groups with two periodic dimensions (d = 3, p = 2):

$$N_{A}(\Lambda) = \left\{ \begin{cases} n_{11} & n_{12} & r_{13} & x_{1} \\ n_{21} & n_{22} & r_{23} & x_{2} \\ 0 & 0 & r_{33} & x_{3} \end{cases} : \begin{vmatrix} n_{11} & n_{12} \\ n_{21} & n_{22} \end{vmatrix} = \pm 1 \wedge r_{33} \neq 0 \wedge r_{ij}, x_{i} \in \mathbb{R} \wedge n_{ij} \in \mathbb{Z} \right\}$$

A different approach to deriving normalizers of crystallographic groups was discussed by Boisen et al.⁹⁹. One of the main differences is that Boisen et al. start from the point group normalizers, noting that the linear part of an element of a space group normalizer must be an element of the normalizer of its point group. This would not be a significant benefit for deriving the subperiodic group normalizers because it would only constrain the *p*-by-*p* submatrix of integers.

2.3 Affine normalizers of subperiodic groups

The problem of computing the normalizer of a group $G \subset E$ will be simplified by considering the quotient of G with respect to its translational subgroup Λ . G is factored by Λ into a set of cosets:

$$G/\Lambda = \{g_1\Lambda, g_2\Lambda, \dots, g_i\Lambda\}$$

where g_1 through g_i is an indexed set of coset representatives (the identity motion will be selected for g_1). Since we are only considering crystallographic subperiodic groups, *i* is finite and equal to the size of the point group of *G*, e.g. the point group of *pmm*2 is *mm*2 which has four elements thus *i*=4 for *G* = *pmm*2. Let *s* denote an element of the affine normalizer of *G*. Since $G = sGs^{-1}$, we may write that

$$G/\Lambda = \{sg_1\Lambda s^{-1}, sg_2\Lambda s^{-1}, \dots, sg_i\Lambda s^{-1}\}$$

As discussed in Section 2, $G = sGs^{-1}$ implies $\Lambda = s\Lambda s^{-1}$. We can therefore substitute $s^{-1}\Lambda s$ for Λ :

$$G/\Lambda = \{ sg_1(s^{-1}\Lambda s)s^{-1}, sg_2(s^{-1}\Lambda s)s^{-1}, \dots, sg_i(s^{-1}\Lambda s)s^{-1} \}$$

which simplifies to

$$G/\Lambda = \{sg_1s^{-1}\Lambda, sg_2s^{-1}\Lambda, \dots, sg_is^{-1}\Lambda\}$$

Thus, if *s* is an element of the normalizer of *G*, $sg_1s^{-1}\Lambda$ through $sg_is^{-1}\Lambda$ is just a permutation of $g_1\Lambda$ through $g_i\Lambda$ that preserves the group law of G/Λ , i.e. an automorphism of G/Λ . Furthermore, this is only true for affine transformations when *s* is an element of the affine normalizer of *G* because *G* is the union of the cosets of G/Λ . Therefore, an affine transformation *s* is an element of the affine normalizer of *G* because *G* is the union of the affine normalizer of *G* if and only if

$$(sg_1s^{-1}\Lambda, sg_2s^{-1}\Lambda, \dots, sg_is^{-1}\Lambda) = \sigma(g_1\Lambda, g_2\Lambda, \dots, g_i\Lambda)$$

for some σ in Aut(G/Λ). This can be further refined by the realization that $g_j\Lambda$ is conjugate to $sg_js^{-1}\Lambda$ in $N_A(\Lambda)$ because $N_A(G) \subset N_A(\Lambda)$ ^{III}. We can therefore limit σ to only those automorphisms of G/Λ which respect this condition. Furthermore, we need only consider a generating set of G/Λ , provided that the generating set is closed under conjugacy in $N_A(\Lambda)$. It is also possible to avoid the difficulty of computing inverses by rearranging the previous equation to the following:

$$(sg_1\Lambda, sg_2\Lambda, \dots, sg_i\Lambda) = \sigma(g_1s\Lambda, g_2s\Lambda, \dots, g_is\Lambda)$$

Determining conjugacy on $N_A(\Lambda)$ is fairly straightforward in Mathematica by setting up the appropriate equations and checking for solutions using the symbolic solver, but may be difficult without comparable software. A much simpler condition is to only consider permutations that exchange elements with identical invariant characteristics, i.e. class functions on $N_A(\Lambda)$ or A (e.g. determinants, traces, eigenvalues, etc.). It is also possible to use canonical forms, if non-primitive glides and possible reorderings of blocks are carefully accounted for.

To summarize, for each subperiodic group G, $N_A(G)$ is solved for by:

ⁱⁱⁱ Note that this is not quite the same as g_j is conjugate to sg_js^{-1} in $N_A(\Lambda)$ because the elements of $g_j\Lambda$ can fall into two separate conjugacy classes of $N_A(\Lambda)$ if some of its elements have no glide components and others have non-primitive glides. In three or fewer dimensions, the glide vector of a crystallographic motion $\{a|\vec{t}\}$ can be calculated by $\vec{t}_{glide} = \frac{\sum_{i=0}^{11} a^i}{12}\vec{t}$ (a consequence of the LCM of the orders allowed by the crystallographic restriction theorem). If a primitive basis is used, then the conjugacy of $\{a|\vec{t}\}\Lambda$ and $s\{a|\vec{t}\}s^{-1}\Lambda$ on $N_A(\Lambda)$ can be checked by comparing the elements of each where the translation components are greater than or equal to zero and less than one.

1. factoring G into a finite set of cosets with respect to Λ ,

2. considering how those cosets may be permuted by elements of $N_A(\Lambda)$, and then

3. solving for the elements of $N_A(\Lambda)$ that are also elements of $N_A(G)$.

2.3.1 Example: L23, pmm2

In this section, we will demonstrate how $N_A(G)$ can be solved for with a specific example: $G = pmm^2$, the 23rd type of layer group. For this group,

$$G/\Lambda = \{\{1|0\}\Lambda, \{2_{001}|0\}\Lambda, \{m_{100}|0\}\Lambda, \{m_{010}|0\}\Lambda\}$$

There are 4! = 24 permutations of G/Λ , but most are not automorphisms and even fewer preserve conjugacy on $N_A(\Lambda)$. Checking the additional permutations is not necessary but will not affect the results. For this group, 24 permutations is computationally tractable but for other groups the number of permutations is too large. For instance, with p6/mmm, $|G/\Lambda| = 24$ and $24! \sim 6 \times 10^{23}$; clearly brute force computing this many permutations is not going to be possible!

The condition that conjugacy on $N_A(\Lambda)$ needs to be preserved means that the only permutations of G/Λ that need to be considered are the identity permutation and the transposition of $\{m_{100}|0\}\Lambda$ and $\{m_{010}|0\}\Lambda$ (in this case, the invariance of the eigenvalues would have been enough to eliminate the other 22 permutations). These two permutations are depicted in Figure 2-2.



Figure 2-2. Possible permutations of G/Λ by conjugation by an affine transformation when G = pmm2.

The blue dotted arrows are the identity permutation, e.g. one of the many values of s that would induce this permutation is $s = \{m_{001}|0\}$. The red dashed arrows are the permutation that swaps $\{m_{100}|0\}\Lambda$ and $\{m_{010}|0\}\Lambda$, e.g. $s = \{4_{001}|0\}$.

Thus, the affine normalizers have to satisfy the conditions (1), (2) and either (3a) or (3b):

(1):
$$s\{1|0\}\Lambda = \{1|0\}s\Lambda$$

(2): $s\{2_{001}|0\}\Lambda = \{2_{001}|0\}s\Lambda$
(3a): $s\{m_{100}|0\}\Lambda = \{m_{100}|0\}s\Lambda$ and $s\{m_{010}|0\}\Lambda = \{m_{010}|0\}s\Lambda$
(3b): $s\{m_{100}|0\}\Lambda = \{m_{010}|0\}s\Lambda$ and $s\{m_{010}|0\}\Lambda = \{m_{100}|0\}s\Lambda$

Putting these into explicit algebraic equations will only be shown for (2). Recalling that $\Lambda = \{\{1|h, k, 0\} : h, k \in \mathbb{Z}\}$ for a primitive basis of a layer group, $s\{2_{001}|0\}\Lambda$ can be written explicitly with matrices as

$$\begin{cases} n_{11} & n_{12} & r_{13} & x_1 \\ n_{21} & n_{22} & r_{23} & x_2 \\ 0 & 0 & r_{33} & x_3 \end{cases} \begin{cases} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & | & 0 \\ 0 & 0 & 1 & 0 \end{cases} \begin{cases} \begin{pmatrix} 1 & 0 & 0 & h \\ 0 & 1 & 0 & | & k \\ 0 & 0 & 1 & 0 \end{pmatrix} : h, k \in \mathbb{Z} \end{cases}$$

which may be simplified to

$$\left\{ \begin{cases} -n_{11} & -n_{12} & r_{13} & -h n_{11} - k n_{12} + x_1 \\ -n_{21} & -n_{22} & r_{23} \mid -h n_{21} - k n_{22} + x_2 \\ 0 & 0 & r_{33} & x_3 \end{cases} : h, k \in \mathbb{Z} \right\}$$

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Similarly $\{2_{001}|0\}$ s Λ may be written:

$$\left\{ \begin{cases} -n_{11} & -n_{12} & -r_{13} & -h \, n_{11} - k \, n_{12} - x_1 \\ -n_{21} & -n_{22} & -r_{23} \mid -h \, n_{21} - k \, n_{22} - x_2 \\ 0 & 0 & r_{33} & x_3 \end{cases} : h, k \in \mathbb{Z} \right\}$$

Accounting for terms that are fixed across the sets, the logical expansion over the components of $s\{2_{001}|0\}\Lambda = \{2_{001}|0\}s\Lambda$ thus simplifies to $r_{13} = -r_{13}$, $r_{23} = -r_{23}$, $\{-h n_{11} - k n_{12} + x_1: h, k \in \mathbb{Z}\} = \{-h n_{11} - k n_{12} - x_1: h, k \in \mathbb{Z}\}$, and $\{-h n_{21} - k n_{22} + x_2: h, k \in \mathbb{Z}\} = \{-h n_{21} - k n_{22} - x_2: h, k \in \mathbb{Z}\}$. This solves to $r_{13} = 0$, $r_{23} = 0$, $2x_1 \in \mathbb{Z}$, and $2x_2 \in \mathbb{Z}$.

Repeating this process for the other conditions gives the solution for the affine normalizer:

$$N_{A}(pmm2) = \begin{cases} \left\{ \begin{array}{cccc} \pm 1 & 0 & 0 & x_{1}/2 \\ 0 & \pm 1 & 0 & |x_{2}/2 \\ 0 & 0 & r_{33} & x_{3} \end{array} \right\}, \begin{cases} 0 & \pm 1 & 0 & x_{1}/2 \\ \pm 1 & 0 & 0 & |x_{2}/2 \\ 0 & 0 & r_{33} & x_{3} \end{array} \right\} : r_{33} \neq 0 \land r_{33}, x_{3} \in \mathbb{R} \land x_{1}, x_{2} \in \mathbb{Z} \end{cases}$$

The values of the ± 1 's are independent. Since $\{\{m_{100}|0\}\Lambda, \{m_{010}|0\}\Lambda\}$ is closed under conjugacy in $N_A(\Lambda)$ and generates G/Λ , it would have been sufficient to use the conditions relating to these.

2.4 Euclidean normalizers of subperiodic groups

Since the Euclidean normalizers are subgroups of the affine normalizers, in order to find the Euclidean normalizer of each subperiodic group G, we need

only consider which elements of each affine normalizer preserve the distance metric M, i.e. which $\{a|\vec{t}\} \in N_A(G)$ satisfy $a^T M a = M$:

$$N_E(G) = \{\{a | \vec{t}\} \in N_A(G) : a^T M a = M\}$$

This expression comes from defining Euclidean length of a column vector v as $d = \sqrt{v^T M v}$. For each symmetry group, there are constraints on the metric that must be satisfied in order for it to be consistent with the symmetry, e.g. in a cubic symmetry group M is the identity matrix times the square of the lattice constant on the standard basis. When these constraints and no others are satisfied, the metric is considered "general". Special metrics that are more constrained than the general metric need to be considered for some of the layer groups.

2.4.1 Example: L1, p1

For p1, the most general type of metric is an oblique metric which is expressed on the standard crystal basis as:

$$\begin{pmatrix} a^2 & ab\cos\gamma & 0\\ ab\cos\gamma & b^2 & 0\\ 0 & 0 & 1 \end{pmatrix}$$

where a and b are the lengths of the unit cell vectors and γ is the angle between them. The "1" in the final position indicates that a vector of unit length and orthogonal to the lattice vectors has been chosen as the arbitrary third basis vector. The affine normalizer of p1 is:

$$N_A(p1) = \begin{cases} \begin{pmatrix} n_{11} & n_{12} & r_{13} & x_1 \\ n_{21} & n_{22} & r_{23} & x_2 \\ 0 & 0 & r_{33} & x_3 \end{pmatrix} : \begin{vmatrix} n_{11} & n_{12} \\ n_{21} & n_{22} \end{vmatrix} = \pm 1 \wedge r_{33} \neq 0 \wedge r_{ij}, x_i \in \mathbb{R} \wedge n_{ij} \in \mathbb{Z} \end{cases}$$
We can find which of these satisfy $a^T M a = M$ by solving for the n_{ij} and r_{ij} values that solve

$$\begin{pmatrix} n_{11} & n_{21} & 0\\ n_{12} & n_{22} & 0\\ r_{13} & r_{23} & r_{33} \end{pmatrix} \begin{pmatrix} a^2 & ab\cos\gamma & 0\\ ab\cos\gamma & b^2 & 0\\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} n_{11} & n_{12} & r_{13}\\ n_{21} & n_{22} & r_{23}\\ 0 & 0 & r_{33} \end{pmatrix} = \begin{pmatrix} a^2 & ab\cos\gamma & 0\\ ab\cos\gamma & b^2 & 0\\ 0 & 0 & 1 \end{pmatrix}$$

for all real values of a, b, and y. The result is

$$\begin{split} & N_E(p1) = \\ & \left\{ \begin{pmatrix} 1 & 0 & 0 & x_1 \\ 0 & 1 & 0 & | & x_2 \\ 0 & 0 & 1 & x_3 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 & x_1 \\ 0 & -1 & 0 & | & x_2 \\ 0 & 0 & 1 & x_3 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 & x_1 \\ 0 & 1 & 0 & | & x_2 \\ 0 & 0 & -1 & x_3 \end{pmatrix}, \begin{pmatrix} -1 & 0 & 0 & x_1 \\ 0 & -1 & 0 & | & x_2 \\ 0 & 0 & -1 & x_3 \end{pmatrix} : x_i \in \mathbb{R} \right\} \end{split}$$

The Hermann-Mauguin symbol for this Euclidean normalizer group is $P^{3}112/m$, which is similar to space group P2/m but with continuous translational symmetry.

For the special case of p1 where the unit cell is square, $\gamma = 90^{\circ}$ and a = b, the metric is

$$\begin{pmatrix} a^2 & 0 & 0 \\ 0 & a^2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

For this special metric, the Euclidean normalizer group of p1 is $P^{3}4/mmm$. The square lattice is invariant under four-fold rotation whereas the oblique lattice was not.

2.5 Normalizer Tables

Using the methods described in this chapter, the affine and Euclidean normalizers of the subperiodic groups were derived and listed. To help validate our methods, the space group affine normalizers were computed and the results matched the listing found on the Bilbao Crystallographic Server. The normalizer tables for the Frieze, layer, and rod groups have been made to resemble the format of the space group and plane group normalizer tables given in the International Tables for Crystallography Vol. A. Each subperiodic group from the International Tables for Crystallography Vol. E¹⁰⁶ is listed sequentially in each table with a number and a Hermann-Mauguin symbol for each. Additionally, for the layer groups, special metric types were considered for cases where the results differ from a general metric.

After the columns specifying the subperiodic group, the Euclidean normalizer is given by a symbol and the basis vectors for the symbol in terms of the subperiodic group's basis vectors. For cases where the Euclidean normalizer is a crystallographic group, this group is given with the standard symbol. For cases where it is not, a generalization of the standard symbol is given, e.g. $N_E(p6/mmm)$ is given as p12/mmm. When the Euclidean normalizer contains continuous translation, a superscript number on the centering symbol denotes how many independent directions are continuous, e.g. $N_E(p4mm)$ contains continuous translation along the rod axis and thus is given as $p^{1}8/mmm$. The standard choice of origin occurred for all Euclidean normalizers of the subperiodic groups except for three: layer groups 52, 62, and 64. In these cases, the symbol for $N_E(G)$ is given as p4/mmm (mmm) to indicate that the origin is at a point with mmm site symmetry rather than the standard origin.

Following the Euclidean normalizer, a set of additional generators are given which, when added to the generators of G, can be used to generate $N_E(G)$. The choice and description of additional generators was made to match

the normalizer tables given in the International Tables for Crystallography Vol. A 98,101.

The final column gives the index of *G* in $N_E(G)$. This is factored in the same way as in the normalizer tables given in the International Tables for Crystallography Vol. A: the first number accounts for additional translational symmetry (we have factored this further into components that are perpendicular and parallel to the periodic subspace of *G*), the number in the second position is 2 if either inversion (rod and layer groups) or two-fold rotation (Frieze groups) is gained, otherwise it is 1, and the number in the final position is the remaining factor once the first two positions are accounted for. In the cases where continuous translation or continuous rotation is gained, ∞ appears in the factored index.

As is the case with the monoclinic and triclinic space groups, the affine normalizers of the subperiodic groups are not isomorphic to the Euclidean normalizers of any specialized metric. It is for this reason that Hermann-Mauguin symbols have not been given for the affine normalizers of the subperiodic groups. Instead, only the matrix representations of the elements of the affine normalizers of the subperiodic groups are listed.

The file "SubperiodicGroupNormalizersMachineReadableFiles.zip" contains the text files with matrix representatives of the elements of the affine and Euclidean normalizers for each subperiodic group. This file is given in the supplemental materials of our *Acta Cryst*. A article on this work⁹⁷. The purpose of

these text files is to allow the matrix representations of $N_E(G)$ and $N_A(G)$ for any subperiodic group G to be easily parsed by a computer program.

Each normalizer listed in these text files starts with a single number on the first line giving the subperiodic group number. In the case of the Euclidean normalizers of the layer groups, the metric is also described on this line. The remaining lines give the augmented matrix representations of the elements of the normalizer flattened onto a single line. Thus for the Frieze group normalizers, there are nine entries on each of these lines which are to be partitioned sequentially into the rows of a 3x3 matrix. For the layer and rod group normalizers, there are sixteen entries on each of these lines which are to be partitioned sequentially into the rows of a 4x4 matrix. The matrix representations are given for the conventional setting only. Elements that differ by a translation of the conventional unit cell are listed by one representative, i.e. every matrix represents itself combined with any integer translation in the periodic subspace. There are non-numeric entries that are a letter followed by a number, such as "r1". These entries represent any real number if the letter is "r", any integer if the letter is "n", and any real number greater than or equal to zero and less than one if the letter is "x". The Mathematica file "Load Zipped SubperiodicGroupNormalizersMachineReadableFiles.nb" has also been provided in the supplemental materials of our Acta Cryst. A article on this work⁹⁷. This file will parse the normalizers directly from the zip file.

2.5.1 Euclidean normalizers of the Frieze groups

Frieze g	group G		Euclidean	normalizer $N_E(G)$	Additional ge	enerators of	$N_E(G)$	
	Hermann-							
	Mauguin					Twofold	Further	Index of G in
No.	symbol	Cell metric	Symbol	Basis vectors	Translations	rotation	generators	$N_E(G)$
1	<i>p</i> 1	General	<i>p</i> ² 2 <i>mm</i>	$\varepsilon_1 \mathbf{a}, \varepsilon_2 \mathbf{b}$	$x_1, 0; 0, x_2$	-x, -y	-x, y	$(\infty_{\parallel} \cdot \infty_{\perp}) \cdot 2 \cdot 2$
2	<i>p</i> 211	General	p2mm	$\frac{1}{2}\mathbf{a},\mathbf{b}$	$\frac{1}{2}, 0$		- <i>x</i> , <i>y</i>	$2 \cdot 1 \cdot 2$
3	p1m1		<i>p</i> ¹ 2 <i>mm</i>	$\frac{1}{2}$ a , ε_2 b	$\frac{1}{2}$, 0; 0, x_2	-x, -y		$(2 \cdot \infty_{\perp}) \cdot 2 \cdot 1$
4	p11m		$p^1 2mm$	$\varepsilon_1 \mathbf{a}, \mathbf{b}$	<i>x</i> ₁ ,0	- <i>x</i> , - <i>y</i>		$\infty_{\parallel} \cdot 2 \cdot 1$
5	p11g		$p^1 2mm$	$\varepsilon_1 \mathbf{a}, \mathbf{b}$	<i>x</i> ₁ ,0	<i>−x, −y</i>		$\infty_{\parallel} \cdot 2 \cdot 1$
6	p2mm		p2mm	$\frac{1}{2}$ a , b	$\frac{1}{2}, 0$			$2 \cdot 1 \cdot 1$
7	p2mg		p2mm	$\frac{1}{2}\mathbf{a},\mathbf{b}$	$\frac{1}{2}$, 0			$2 \cdot 1 \cdot 1$

Table 2-1. Euclidean normalizers of the Frieze groups.

2.5.2 Euclidean normalizers of the layer groups

Laye	r Group G		Euclidean no	rmalizer $N_E(G)$	Additional generators	of $N_E(G)$		
	Hermann	Cell Metric						
	-Mauguin					Inver-	Further	Index of G in
No.	symbol		Symbol	Basis vectors	Translations	sion	generators	$N_E(G)$
1	<i>p</i> 1	General Metric	P ³ 112/m	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0; 0, 0, x_3$	(0,0,0)	-x,-y,z	$(\infty_{\perp} \infty_{\parallel}^2) \cdot 2 \cdot 2$
		$a < b, \gamma = 90^{\circ}$	P ³ mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$x_1, 0,0; 0, x_2, 0; 0,0, x_3$	(0,0,0)	-x,-y,z;-x,y,-z	$(\infty_{\perp} \infty_{\parallel}^2) \cdot 2 \cdot 4$
		$a = b, \gamma = 90^{\circ}$	P^34/mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$x_1, 0,0; 0, x_2, 0; 0,0, x_3$	(0,0,0)	-y,x,z;-x,-y,z;-x,y,-z	$(\infty_{\perp} \infty_{\parallel}^2) \cdot 2 \cdot 8$
		$2\cos\gamma = \frac{-a}{h}, 90^{\circ} < \gamma < 120^{\circ}$	C ³ mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 (\frac{1}{2}\boldsymbol{a} + \boldsymbol{b}), \varepsilon_3 \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0; 0, 0, x_3$	(0,0,0)	-x,-y,z;-x+y,y,z	$(\infty_{\perp} \infty_{\parallel}^2) \cdot 2 \cdot 4$
		$a = b,90^{\circ} < \gamma < 120^{\circ}$	C ³ mmm	$\frac{\varepsilon_1}{2}(a+b), \frac{\varepsilon_2}{2}(b-a), \varepsilon_3 c$	$x_1, 0, 0; 0, x_2, 0; 0, 0, x_3$	(0,0,0)	-x,-y,z;-y,-x,z	$(\infty_{\perp} \infty_{\parallel}^2) \cdot 2 \cdot 4$
		$a = b, \gamma = 120^{\circ}$	P ³ 6/mmm	$\varepsilon_1^2 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0; 0, 0, x_3$	(0,0,0)	-y,x-y,z;-x,-y,z;y,x,z	$(\infty_{\perp} \infty_{\parallel}^2) \cdot 2 \cdot 12$
2	$p\overline{1}$	General Metric	p112/m	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		$a < b, \gamma = 90^{\circ}$	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x,-y,z;-x,y,-z	$4 \cdot 1 \cdot 4$
		$a = b, \gamma = 90^{\circ}$	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y,x,z;-x,y,-z	$4 \cdot 1 \cdot 8$
		$2\cos\gamma = \frac{-a}{b}, 90^{\circ} < \gamma < 120^{\circ}$	сттт	$\frac{1}{2}a, \frac{1}{2}a + b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x+y,y,z;-y,-x,-z	$4 \cdot 1 \cdot 4$
		$a = b,90^{\circ} < \gamma < 120^{\circ}$	сттт	$\frac{1}{2}(a+b),\frac{1}{2}(b-a), C$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y,x,z;-x+y,y,z	$4 \cdot 1 \cdot 4$
		$a = b, \gamma = 120^{\circ}$	p6/mmm	a, b, c			-y,x-y,z;-x,-y,z;y,x,z	$1 \cdot 1 \cdot 12$

Table 2-2. Euclidean normalizers of the layer groups No. 1 through No. 7.

3	<i>p</i> 112	General Metric	P ¹ 112/m	$\frac{1}{2}a,\frac{1}{2}b,\varepsilon_3c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)		$(\infty_{\perp}4) \cdot 2 \cdot 1$
		$a < b, \gamma = 90^{\circ}$	P ¹ mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\varepsilon_{3}\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)	-x,y,-z	$(\infty_{\perp}4) \cdot 2 \cdot 2$
		$a = b, \gamma = 90^{\circ}$	P ¹ 4/mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\varepsilon_{3}\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)	-y,x,z;-x,y,-z	$(\infty_{\perp}4) \cdot 2 \cdot 4$
		$2\cos\gamma = \frac{-a}{b}, 90^\circ < \gamma < 120^\circ$	C ¹ mmm	$\frac{1}{2}a, \frac{1}{2}a + b, \varepsilon_3c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)	-x+y,y,z	$(\infty_{\perp}4) \cdot 2 \cdot 2$
		$a = b,90^{\circ} < \gamma < 120^{\circ}$	C ¹ mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a), \mathcal{E}_3C$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)	-y,-x,-z	$(\infty_{\perp}4) \cdot 2 \cdot 2$
		$a=b, \gamma=120^{\circ}$	P ¹ 6/mmm	α , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)	-y,x-y,z;y,x,-z	$(\infty_{\perp}1) \cdot 2 \cdot 6$
4	p11m	General Metric	p ² 112/m	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)		$(1\infty_{\parallel}^2) \cdot 2 \cdot 1$
		$a < b, \gamma = 90^{\circ}$	p ² mmm	$\varepsilon_1 \pmb{a}, \varepsilon_2 \pmb{b}, \pmb{c}$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	-х,у,-z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
		$a = b, \gamma = 90^{\circ}$	p ² 4/mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	-y,x,z;-x,y,-z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 4$
		$2\cos\gamma = \frac{-a}{b}, 90^{\circ} < \gamma < 120^{\circ}$	c²mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \left(\frac{1}{2}\boldsymbol{a} + \boldsymbol{b}\right), \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	-x+y,y,z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
		$a = b,90^{\circ} < \gamma < 120^{\circ}$	c²mmm	$\frac{\varepsilon_1}{2}(a+b), \frac{\varepsilon_2}{2}(b-a), c$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	-y,-x,-z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
		$a=b, \gamma=120^{\circ}$	p²6/mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	<i>x</i> ₁ , 0,0; 0, <i>x</i> ₂ , 0	(0,0,0)	-y,x-y,z;y,x,-z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 6$

5	p11a	General Metric	$p^2 112/m$	$\varepsilon_1 \pmb{a}$, $\varepsilon_2 \pmb{b}$, \pmb{c}	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)		$(1\infty_{\parallel}^2) \cdot 2 \cdot 1$
		$a < b, \gamma = 90^{\circ}$	p²mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	-x,y,-z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
		$a = b, \gamma = 90^{\circ}$	c ² mmm	$\varepsilon_1 \pmb{a}, \varepsilon_2 \pmb{b}, \pmb{c}$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	-x,y,-z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
		$2\cos\gamma = \frac{-a}{b}, 90^{\circ} < \gamma < 120^{\circ}$	c²mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2(\frac{1}{2}\boldsymbol{a} + \boldsymbol{b}), \boldsymbol{c}$		(0,0,0)	х-у,-у,z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
		$a = b,90^{\circ} < \gamma < 120^{\circ}$	c²mmm	$\frac{\varepsilon_1}{2}(\boldsymbol{a}+\boldsymbol{b}),\frac{\varepsilon_2}{2}(\boldsymbol{b})$	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	-y,-x,z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
		$a = b, \gamma = 120^{\circ}$	c²mmm	- a), c	$x_1, 0, 0; 0, x_2, 0$	(0,0,0)	х-у,-у,-z	$(1\infty_{\parallel}^2) \cdot 2 \cdot 2$
				$\varepsilon_1 \boldsymbol{a}, \varepsilon_2(\frac{1}{2}\boldsymbol{a} + \boldsymbol{b}), \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0$			
6	p112/m	General Metric	p112/m	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		$a < b, \gamma = 90^{\circ}$	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-X,y,-Z	4 · 1 · 2
		$a=b,\gamma=90^{\circ}$	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y,x,z;-x,y,-z	$4 \cdot 1 \cdot 4$
		$2\cos\gamma = \frac{-a}{b}, 90^{\circ} < \gamma < 120^{\circ}$	сттт	$\frac{1}{2}a, \frac{1}{2}a + b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x+y,y,z	4 · 1 · 2
		$a = b,90^{\circ} < \gamma < 120^{\circ}$	сттт	$\frac{1}{2}(a+b),\frac{1}{2}(b-a), C$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y,-x,-z	4 · 1 · 2
		$a = b, \gamma = 120^{\circ}$	p6/mmm	2 2 a, b, c			-y,x,z ;-x+y,y,z	$1 \cdot 1 \cdot 3$

7	p112/a	General Metric	p112/m	$\frac{1}{2}a,\frac{1}{2}b,c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		$4 \cdot 1 \cdot 1$
		$a < b, \gamma = 90^{\circ}$	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	-x,y,-z	4 · 1 · 2
		$a=b,\gamma=90^{\circ}$	сттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	-x,y,-z	4 · 1 · 2
		$2\cos\gamma = \frac{-a}{b}, 90^{\circ} < \gamma < 120^{\circ}$	сттт	$\frac{1}{2}a, \frac{1}{2}a + b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	x-y,-y,z	4 · 1 · 2
		$a = b,90^{\circ} < \gamma < 120^{\circ}$	сттт	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	-y,-x,z	4 · 1 · 2
		$a=b,\gamma=120^{\circ}$	сттт	$\frac{1}{2}a, \frac{1}{2}a + b, c$		x-y,-y,-z	1 · 1 · 2

Layer	Group G		Euclidean norma	lizer $N_E(G)$	Additional generator	s of $N_E(G$;)	
	Hermann-	Cell Metric						
	Mauguin					Inver-		Index of G in
No.	symbol		Symbol	Basis vectors	Translations	sion	Further generators	$N_E(G)$
8	<i>p</i> 211	General Metric	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \frac{1}{2} \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; \frac{1}{2}, 0, 0$	(0,0,0)	-x, y, -z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
		a = b	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \frac{1}{2} \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; \frac{1}{2}, 0, 0$	(0,0,0)	-x, y, -z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
9	p2 ₁ 11	General Metric	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \frac{1}{2} \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; \frac{1}{2}, 0, 0$	(0,0,0)	-x, y, -z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
		a = b	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \frac{1}{2} \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; \frac{1}{2}, 0, 0$	(0,0,0)	-x, y, -z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
10	c211	General Metric	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \frac{1}{2} \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; \frac{1}{2}, 0, 0$	(0,0,0)	-x, y, -z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
		a = b	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \frac{1}{2} \boldsymbol{b}, \boldsymbol{c}$	$x_1, 0, 0; \frac{1}{2}, 0, 0$	(0,0,0)	-x, y, -z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
11	pm11	General Metric	P ² mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0; 0,0, x_3	(0,0,0)	-x, y, -z	$(\infty_{\perp}\infty_{\parallel})\cdot 2\cdot 2$
		a = b	P ² mmm	$\frac{1}{2}\boldsymbol{a},\varepsilon_2\boldsymbol{b},\varepsilon_3\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0; 0,0, x_3	(0,0,0)	-x, y, -z	$(\infty_{\perp} \infty_{\parallel}) \cdot 2 \cdot 2$
12	<i>pb</i> 11	General Metric	P ² mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0; 0,0, x_3	(0,0,0)	-x, y, -z	$(\infty_{\perp}\infty_{\parallel}) \cdot 2 \cdot 2$
		a = b	P ² mmm	$\frac{1}{2}a, \varepsilon_2 b, \varepsilon_3 c$	$\frac{1}{2}$, 0,0; 0, x_2 , 0; 0,0, x_3	(0,0,0)	-x, y, -z	$(\infty_{\perp}\infty_{\parallel}) \cdot 2 \cdot 2$
13	<i>cm</i> 11	General Metric	P ² mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0; 0,0, x_3	(0,0,0)	- <i>x</i> , <i>y</i> , - <i>z</i>	$(\infty_{\perp}\infty_{\parallel}) \cdot 2 \cdot 2$

Table 2-3. Euclidean normalizers of the layer groups No. 8 through No 80.

		a = b	P ² mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0; 0,0, x_3	(0,0,0)	-x, y, -z	$(\infty_{\perp}\infty_{\parallel}) \cdot 2 \cdot 2$
14	p2/m11	General Metric	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	4 · 1 · 2
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
15	p2 ₁ /m11	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
		a = b	pmmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
16	p2/b11	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
17	p2 ₁ /b11	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
18	c2/m11	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
		a = b	pmmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-x, y, -z	$4 \cdot 1 \cdot 2$
19	p222	General Metric	рттт	$\frac{1}{2}a,\frac{1}{2}b,c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)		$4 \cdot 2 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)	-y, x, z	4 · 2 · 2
20	p2 ₁ 22	General Metric	рттт	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)		$4 \cdot 2 \cdot 1$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)		$4 \cdot 2 \cdot 1$

21	<i>p</i> 2 ₁ 2 ₁ 2	General Metric	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)		$4 \cdot 2 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)	-y, x, z	$4 \cdot 2 \cdot 2$
22	c222	General Metric	рттт	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)		$4 \cdot 2 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0	(0,0,0)	-y, x, z	4 · 2 · 2
23	pmm2	General Metric	P ¹ mmm	$\frac{1}{2}a,\frac{1}{2}b,\varepsilon_3c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)		$(\infty_{\perp}4) \cdot 2 \cdot 1$
		a = b	P^14/mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\varepsilon_{3}\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)	-y, x, z	$(\infty_{\perp}4) \cdot 2 \cdot 2$
24	pma2	General Metric	P^1mmm	$\frac{1}{2}a,\frac{1}{2}b,\varepsilon_3c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)		$(\infty_{\perp}4) \cdot 2 \cdot 1$
		a = b	P^1mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\varepsilon_{3}\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)		$(\infty_{\perp}4) \cdot 2 \cdot 1$
25	pba2	General Metric	P^1mmm	$\frac{1}{2}a,\frac{1}{2}b,\varepsilon_3c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)		$(\infty_{\perp}4) \cdot 2 \cdot 1$
		a = b	P^14/mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\varepsilon_{3}\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)	-y, x, z	$(\infty_{\perp}4) \cdot 2 \cdot 2$
26	cmm2	General Metric	P^1mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\varepsilon_{3}\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)		$(\infty_{\perp}4) \cdot 2 \cdot 1$
		a = b	P^14/mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\varepsilon_{3}\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0; 0,0, x_3	(0,0,0)	-y, x, z	$(\infty_{\perp}4) \cdot 2 \cdot 2$
27	pm2m	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)		$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)		$(1\infty_{\parallel}) \cdot 2 \cdot 1$
28	<i>pm</i> 2 ₁ <i>b</i>	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)		$(1\infty_{\parallel}) \cdot 2 \cdot 1$

		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
29	pb2 ₁ b	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
30	pb2b	General Metric	p^1mmm	$\frac{1}{2}a, \varepsilon_2 b, c$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
31	pm2a	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
32	pm2 ₁ n	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
33	pb2 ₁ a	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
34	pb2n	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
35	cm2m	General Metric	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)	$(1\infty_{\parallel}) \cdot 2 \cdot 1$

36	cm2e	General Metric	p^1mmm	$\frac{1}{2}a, \varepsilon_2 b, c$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)		$(1\infty_{\parallel}) \cdot 2 \cdot 1$
		a = b	p^1mmm	$\frac{1}{2}\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, x_2 , 0	(0,0,0)		$(1\infty_{\parallel}) \cdot 2 \cdot 1$
37	pmmm	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y, x, z	$4 \cdot 1 \cdot 2$
38	ртаа	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
39	pban	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y, x, z	$4 \cdot 1 \cdot 2$
40	ртат	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
41	ртта	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
42	pman	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
43	pbaa	General Metric	pmmm	$\frac{1}{2}a,\frac{1}{2}b,c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$

		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			4 · 1 · 1
44	pbam	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y, x, z	$4 \cdot 1 \cdot 2$
45	pbma	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	pmmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
46	pmmn	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$4 \cdot 1 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y, x, z	4 · 1 · 2
47	сттт	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$2 \cdot 1 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}\boldsymbol{a},\frac{1}{2}\boldsymbol{b},\boldsymbol{c}$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		-y, x, z	$2 \cdot 1 \cdot 2$
48	стте	General Metric	рттт	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0			$2 \cdot 1 \cdot 1$
		a = b	p4/mmm	$\frac{1}{2}a, \frac{1}{2}b, c$	$\frac{1}{2}$, 0,0; 0, $\frac{1}{2}$, 0		$-y + \frac{1}{4}, x + \frac{1}{4}, z$	$2 \cdot 1 \cdot 2$
49	<i>p</i> 4		P^14/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),\varepsilon_3c$	$0,0,x_3;\frac{1}{2},\frac{1}{2},0$	(0,0,0)	-x, y, -z	$(\infty_{\perp}2) \cdot 2 \cdot 2$
50	$p\overline{4}$		p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)	-x, y, -z	2 · 2 · 2
51	<i>p</i> 4/ <i>m</i>		p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$		-x, y, -z	2 · 1 · 2

52	p4/n	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$		-x, y, -z	$2 \cdot 1 \cdot 2$
		(mmm)					
53	<i>p</i> 422	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)		2 · 2 · 1
54	p42 ₁ 2	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)		$2 \cdot 2 \cdot 1$
55	p4mm	P ¹ 4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),\varepsilon_3c$	$0,0,x_3;\frac{1}{2},\frac{1}{2},0$	(0,0,0)		$(\infty_{\perp}2) \cdot 2 \cdot 1$
56	p4bm	P ¹ 4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),\varepsilon_3c$	$0,0, x_3; \frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)		$(\infty_{\perp}2) \cdot 2 \cdot 1$
57	p42m	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)		2 · 2 · 1
58	$p\overline{4}2_1m$	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)		2 · 2 · 1
59	p4m2	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)		2 · 2 · 1
60	p4b2	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$	(0,0,0)		2 · 2 · 1
61	p4/mmm	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$			2 · 1 · 1
62	p4/nbm	p4/mmm (mmm)	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$			2 · 1 · 1

63	p4/mbm	p4/mmm	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$			2 · 1 · 1
64	p4/nmm	p4/mmm (mmm)	$\frac{1}{2}(a+b),\frac{1}{2}(b-a),c$	$\frac{1}{2}, \frac{1}{2}, 0$			2 · 1 · 1
65	<i>p</i> 3	P ¹ 6/mmm	$\frac{\frac{1}{3}(2a-b),\frac{1}{3}(b)}{-a},\epsilon_3c$	$\frac{2}{3}, \frac{1}{3}, 0$	(0,0,0)	-x, -y, z; y, x, -z	(∞ _⊥ 3) · 2 · 4
66	$p\overline{3}$	p6/mmm	a, b, c			-x, -y, z; y, x, -z	$1 \cdot 1 \cdot 4$
67	p312	p6/mmm	$\frac{1}{3}(2a-b),\frac{1}{3}(b-a),c$	$\frac{2}{3}, \frac{1}{3}, 0$	(0,0,0)	-x, -y, z	3 · 2 · 2
68	<i>p</i> 321	p6/mmm	a, b, c		(0,0,0)	-x, -y, z	1 · 2 · 2
69	p3m1	P ¹ 6/mmm	$\frac{\frac{1}{3}(2a-b),\frac{1}{3}(b)}{-a},\epsilon_3c$	$0,0,x_3; \frac{2}{3},\frac{1}{3},0$	(0,0,0)	-x, -y, z	$(\infty_{\perp}3) \cdot 2 \cdot 2$
70	p31m	P ¹ 6/mmm	a , b , ϵ_3 c	0,0, <i>x</i> ₃	(0,0,0)	-x, -y, z	$(\infty_{\perp}1) \cdot 2 \cdot 2$
71	$p\overline{3}1m$	p6/mmm	a, b, c			-x, -y, z	1 · 1 · 2
72	$p\overline{3}m1$	p6/mmm	a, b, c			-x, -y, z	1 · 1 · 2
73	<i>p</i> 6	P ¹ 6/mmm	a , b , ϵ_3 c	0,0, <i>x</i> ₃	(0,0,0)	<i>y</i> , <i>x</i> , − <i>z</i>	$(\infty_{\perp}1) \cdot 2 \cdot 2$

74	p6	p6/mmm	$\frac{1}{3}(2a-b),\frac{1}{3}(b)$	$\frac{2}{3}, \frac{1}{3}, 0$	(0,0,0)	<i>y</i> , <i>x</i> , − <i>z</i>	3 · 2 · 2
			- a), c				
75	p6/m	p6/mmm	a, b, c			<i>y</i> , <i>x</i> , − <i>z</i>	1 · 1 · 2
76	<i>p</i> 622	p6/mmm	a, b, c		(0,0,0)		1 · 2 · 1
77	p6mm	P ¹ 6/mmm	$\boldsymbol{a}, \boldsymbol{b}, \epsilon_3 \boldsymbol{c}$	0,0, <i>x</i> ₃	(0,0,0)		$(\infty_{\perp}1) \cdot 2 \cdot 1$
78	p6m2	p6/mmm	$\frac{1}{3}(2a-b),\frac{1}{3}(b)$	$\frac{2}{3}, \frac{1}{3}, 0$	(0,0,0)		3 · 2 · 1
			- a), c				
79	p62m	p6/mmm	a, b, c		(0,0,0)		1 · 2 · 1
80	p6/mmm	p6/mmm	a, b, c				1 · 1 · 1

2.5.3 Euclidean normalizers of the rod groups

Rod	Group G	Euclidean normalizer $N_E(G)$		Additional gen	erators of N	$_{E}(G)$	
No.	Hermann- Mauguin symbol	Symbol	Basis vectors	Translations	Inversion	Further generators	Index of G in $N_E(G)$
1	<i>p</i> 1	P ³ ∞/mmm	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	x ₁ , 0,0; 0, x ₂ , 0; 0,0, x ₃	(0,0,0)	Continuous rotation; —x, y, z	$(\infty_{\perp}^2 \infty_{\parallel}) \cdot 2 \cdot \infty$
2	$p\overline{1}$	$p\infty/mmm$	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		Continuous rotation; —x, y, z	2 · 1 · ∞
3	p211	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \boldsymbol{b}, \frac{1}{2}\boldsymbol{c}$	$x_1, 0, 0; 0, 0, \frac{1}{2}$	(0,0,0)	-x, -y, z	$(\infty_{\perp}2) \cdot 2 \cdot 2$
4	<i>p</i> m11	p^2mmm	$\boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	0, <i>x</i> ₂ , 0; 0,0, <i>x</i> ₃	(0,0,0)	- <i>x</i> , - <i>y</i> , <i>z</i>	$(\infty_{\perp}\infty_{\parallel}) \cdot 2 \cdot 2$
5	<i>pc</i> 11	p^2mmm	$a, \varepsilon_2 b, \varepsilon_3 c$	$0, x_2, 0;$ $0, 0, x_3$	(0,0,0)	-x, -y, z	$(\infty_{\perp} \infty_{\parallel}) \cdot 2 \cdot 2$

Table 2-4. Euclidean normalizers of the rod groups.

6	p2/m11	pmmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		- <i>x</i> , - <i>y</i> , <i>z</i>	2 · 1 · 2
7	p2/c11	pmmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		-x, -y, z	2 · 1 · 2
8	p112	$p^{1}\infty/mmm$	a , b , ε ₃ c	0,0, x ₃	(0,0,0)	Continuous rotation; —x, y, z	$(1\infty_{\parallel}) \cdot 2 \cdot \infty$
9	\$p112_1	$p^{1}\infty/mmm$	a , b , ε ₃ c	0,0, x ₃	(0,0,0)	Continuous rotation; —x, y, z	$(1\infty_{\parallel}) \cdot 2 \cdot \infty$
10	p11m	$p^2\infty/mmm$	$\varepsilon_1 \boldsymbol{a}, \varepsilon_2 \boldsymbol{b}, \frac{1}{2} \boldsymbol{c}$	$x_1, 0, 0; 0, x_2, 0;$ $0, 0, \frac{1}{2}$	(0,0,0)	Continuous rotation; -x, y, z	$(\infty_{\perp}^2 2) \cdot 2 \cdot \infty$
11	p112/m	$p\infty/mmm$	$a, b, \frac{1}{2}c$	$0,0\frac{1}{2}$		Continuous rotation; —x, y, z	2 · 1 · ∞
12	p112 ₁ /m	$p\infty/mmm$	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		Continuous rotation; —x, y, z	$2 \cdot 1 \cdot \infty$
13	p222	₽4/mmm	a , b , $\frac{1}{2}$ c	$0,0,\frac{1}{2}$	(0,0,0)	-y, x, z	2 · 2 · 2
14	p2221	$p4_2/mmc$	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)	-y, x, z	2 · 2 · 2
15	pmm2	p^14/mmm	α , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)	-y, x, z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
16	pcc2	p^14/mmm	α , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)	- <i>y</i> , <i>x</i> , <i>z</i>	$(1\infty_{\parallel}) \cdot 2 \cdot 2$

17	pmc2 ₁	p^1mmm	a , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)		$(1\infty_{\parallel}) \cdot 2 \cdot 1$
18	p2mm	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \boldsymbol{b}, \frac{1}{2} \boldsymbol{c}$	$x_1, 0, 0; 0, 0, \frac{1}{2}$	(0,0,0)		$(\infty_{\perp}2) \cdot 2 \cdot 1$
19	p2cm	p^1mmm	$\varepsilon_1 \boldsymbol{a}, \boldsymbol{b}, \frac{1}{2}\boldsymbol{c}$	$x_1, 0, 0; 0, 0, \frac{1}{2}$	(0,0,0)		$(\infty_{\perp}2) \cdot 2 \cdot 1$
20	pmmm	p4/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		- <i>y</i> , <i>x</i> , <i>z</i>	2 · 1 · 2
21	рсст	p4/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		-y, x, z	2 · 1 · 2
22	ртст	pmmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$			2 · 1 · 1
23	<i>p</i> 4	$p^{1}\infty/mmm$	$a, b, \varepsilon_3 c$	0,0, x ₃	(0,0,0)	Continuous rotation; x, -y, -z	$(1\infty_{\parallel})\cdot 2\cdot\infty$
24	<i>p</i> 4 ₁	$p^1 \infty 22$	$a, b, \varepsilon_3 c$	0,0, <i>x</i> ₃		Continuous rotation; x, -y, -z	$(1\infty_{\parallel})\cdot 1\cdot\infty$
25	\$P42	$p^{1}\infty/mmm$	$\boldsymbol{a}, \boldsymbol{b}, \varepsilon_3 \boldsymbol{c}$	0,0, x ₃	(0,0,0)	Continuous rotation; —x, y, z	$(1\infty_{\parallel}) \cdot 2 \cdot \infty$
26	$\mathcal{P}4_3$	$p^{1}\infty 22$	$a, b, \varepsilon_3 c$	0,0, <i>x</i> ₃		Continuous rotation; x, -y, -z	$(1\infty_{\parallel}) \cdot 1 \cdot \infty$
27	₽Ā	p^{∞}/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)	Continuous rotation; —x, y, z	$2 \cdot 2 \cdot \infty$

28	p4/m	p^{∞}/mmm	$a,b,\frac{1}{2}c$	$0,0,\frac{1}{2}$		Continuous rotation; -x, y, z	$2 \cdot 1 \cdot \infty$
29	$p4_2/m$	p^{∞}/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		Continuous rotation; -x, y, z	2 · 1 · ∞
30	p422	p8/mmm	a , b , $\frac{1}{2}$ c	$0, 0, \frac{1}{2}$	(0,0,0)	$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	2 · 2 · 2
31	\$\$p4122	\$p8222	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	2 · 1 · 2
32	\$\$p4222	p8 ₄ /mmc	$a, b, \frac{1}{2}c$	$0, 0, \frac{1}{2}$	(0,0,0)	$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	2 · 2 · 2
33	\$\$P4322	\$\$\$e22	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	2 · 1 · 2
34	p4mm	p^18/mmm	a , b , ε ₃ c	0,0, x ₃	(0,0,0)	$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
35	<i>p</i> 4 ₂ <i>mc</i>	p^14/mmm	α , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)		$(\infty_{\parallel}1) \cdot 2 \cdot 1$
36	p4cc	p^18/mmm	α , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)	$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
37	₽42m	p4/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)		2 · 2 · 1
38	₽42c	p4/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)		2 · 2 · 1
39	p4/mmm	p8/mmm	a , b , $\frac{1}{2}$ c	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	2 · 1 · 2

40	p4/mcc	p8/mmm	$a, b, \frac{1}{2}c$	$0, 0, \frac{1}{2}$		$\frac{1}{\sqrt{2}}x - \frac{1}{\sqrt{2}}y, \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y, z$	2 · 1 · 2
41	\$\$P42/mmc	p4/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$			2 · 1 · 1
42	<i>p</i> 3	$p^{1}\infty/mmm$	α , b , ε ₃ c	0,0, x ₃	(0,0,0)	Continuous rotation; —x, y, z	$(1\infty_{\parallel}) \cdot 2 \cdot \infty$
43	\$P31	$p^1 \infty 22$	α , b , ε ₃ c	0,0, <i>x</i> ₃		Continuous rotation; x,-y,-z	$(1\infty_{\parallel})\cdot 1\cdot\infty$
44	\$P32	$p^1 \infty 22$	a , b , ε ₃ c	0,0, x ₃		Continuous rotation; x, -y, -z	$(1\infty_{\parallel})\cdot 1\cdot\infty$
45	₽3	p^{∞}/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		Continuous rotation; —x, y, z	$2 \cdot 1 \cdot \infty$
46	p312	<i>p</i> 6/mmm	$\frac{1}{3}(2a+b),$ $\frac{1}{3}(-a+b),\frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)	- <i>x</i> , - <i>y</i> , <i>z</i>	2 · 2 · 2
47	\$3 ₁ 12	p6 ₂ 22	$\frac{\frac{1}{3}(2a+b)}{\frac{1}{3}(-a+b),\frac{1}{2}c}$	$0,0,\frac{1}{2}$		-x, -y, z	2 · 1 · 2

48	\$p3212	\$p6422	$\frac{\frac{1}{3}(2a+b),}{\frac{1}{3}(-a+b),\frac{1}{2}c}$	$0,0,\frac{1}{2}$		-x, -y, z	2 • 1 • 2
49	p3m1	p^16/mmm	a , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)	-x, -y, z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
50	p3c1	p ¹ 6/mmm	a , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)	-x, -y, z	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
51	$p\bar{3}m1$	p6/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		-x, -y, z	2 · 1 · 2
52	₽3c1	₽6/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		-x, -y, z	2 · 1 · 2
53	<i>p</i> 6	$p^{1}\infty/mmm$	$a, b, \varepsilon_3 c$	0,0, x ₃	(0,0,0)	Continuous rotation; -x, y, z	$(1\infty_{\parallel})\cdot 2\cdot\infty$
54	p_{6_1}	$p^1 \infty 22$	a , b , ε ₃ c	0,0, <i>x</i> ₃		Continuous rotation; x, -y, -z	$(1\infty_{\parallel})\cdot 1\cdot\infty$
55	$p6_2$	$p^{1}\infty 22$	a , b , ε ₃ c	0,0, x ₃		Continuous rotation; x, -y, -z	$(1\infty_{\parallel}) \cdot 1 \cdot \infty$
56	p6 ₃	$p^{1}\infty/mmm$	$a, b, \varepsilon_3 c$	0,0, <i>x</i> ₃	(0,0,0)	Continuous rotation; —x, y, z	$(1\infty_{\parallel}) \cdot 2 \cdot \infty$
57	p_{6_4}	$p^{1}\infty 22$	a , b , ε ₃ c	0,0, <i>x</i> ₃		Continuous rotation; x, -y, -z	$(1\infty_{\parallel})\cdot 1\cdot\infty$

58	p_{6_5}	$p^{1}\infty 22$	α , b , ε ₃ c	0,0, <i>x</i> ₃		Continuous rotation; x, -y, -z	$(1\infty_{\parallel})\cdot 1\cdot\infty$
59	₽Ē	p^{∞}/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)	Continuous rotation; —x, y, z	$2 \cdot 2 \cdot \infty$
60	<i>p</i> 6/m	p^{∞}/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		Continuous rotation; —x, y, z	2 · 1 · ∞
61	₽63/m	p^{∞}/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		Continuous rotation; —x, y, z	$2 \cdot 1 \cdot \infty$
62	<i>p</i> 622	p12/mmm	<i>a</i> , <i>b</i> , $\frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)	$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 2 · 2
63	\$p6122	\$p12222	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 1 · 2
64	\$p6222	\$p12422	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 1 · 2
65	\$p6322	p12 ₆ /mmc	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)	$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 2 · 2
66	\$p6422	p12 ₈ 22	a , b , $\frac{1}{2}$ c	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 1 · 2
67	\$\$p6522	p12 ₁₀ 22	a , b , $\frac{1}{2}$ c	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 1 · 2

68	р6тт	$p^1 12/mmm$	a , b , ε ₃ c	0,0, x ₃	(0,0,0)	$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
69	р6сс	p^1 12/mmm	$a, b, \varepsilon_3 c$	0,0, <i>x</i> ₃	(0,0,0)	$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	$(1\infty_{\parallel}) \cdot 2 \cdot 2$
70	р6 ₃ тс	p^16/mmm	α , b , ε ₃ c	0,0, <i>x</i> ₃	(0,0,0)		$(1\infty_{\parallel}) \cdot 2 \cdot 1$
71	₽ 6 m2	p6/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)		2 · 2 · 1
72	₽Ēc2	p6/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$	(0,0,0)		2 · 2 · 1
73	p6/mmm	p12/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 1 · 2
74	p6/mcc	p12/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$		$\frac{1}{\sqrt{3}}x - \frac{2}{\sqrt{3}}y, \frac{2}{\sqrt{3}}x - \frac{1}{\sqrt{3}}y, z$	2 · 1 · 2
75	p6/mmc	p6/mmm	$a, b, \frac{1}{2}c$	$0,0,\frac{1}{2}$			2 · 1 · 1

Chapter 3

Double antisymmetry groups

The material in Sections 3.1 through 3.16 is primarily from "Double antisymmetry and the rotation-reversal space groups" by Brian K. VanLeeuwen (myself), Venkatraman Gopalan, and Daniel B. Litvin published in Acta Crystallographica Section A³⁷. Text describing applications to rotation-reversal symmetry has been updated to describe applications to distortion symmetry. Also, additional and supplemental material not published in the main text of the article is given in this chapter. Section 3.17 is adapted from ³⁶ "Crystallographic data of double antisymmetry space groups" by Mantao Huang, Brian K. VanLeeuwen, Daniel B. Litvin, and Venkatraman Gopalan and again is updated to distortion symmetry.

3.1 Introduction

Double antisymmetry space groups are among the generalizations of the crystallographic groups which began with Heesch¹⁰⁷ and Shubnikov¹⁰⁸ and continued to include a myriad of generalizations under various names as antisymmetry groups, cryptosymmetry groups, quasisymmetry groups, color groups and metacrystallographic groups (see reviews by Koptsik¹⁰⁹, Zamorzaev & Palistrant¹¹⁰, Opechowski¹⁰⁰, and Zamorzaev¹¹¹). Only some of these groups have been explicitly listed, e.g. the black and white space groups ^{112,113} and various

multiple antisymmetry¹¹⁴ and color groups¹¹⁵. While no explicit listing of the double antisymmetry space groups has been given, the number of these groups, and other generalizations of the crystallographic groups, have been calculated^{110,114,116-123}.

In this chapter, first, double antisymmetry space groups will be defined and which of these groups will be explicitly tabulated will be specified. This is followed by the details of the procedure used in their tabulation. Then the format of the tables listing these groups is given. Then there will be example diagrams of double antisymmetry space groups (Figure 3-6: No. 8543 C2'/m*, Figure 3-7: No. 16490 I4*/mm'm'*, and Figure 3-8: No. 13461 Ib'*c'a').

Zamorzaev & Palistrant¹¹⁰ have calculated not only the total number of types of double antisymmetry space groups, but they have also specified the number in sub-categories. Errors in these numbers have been found. Consequently, the total number of types of groups is different than calculated by Zamorzaev & Palistrant. This is discussed in Section 3.11.

3.2 Double Antisymmetry Space Groups

Space groups, in this chapter, will be limited to the conventional threedimensional crystallographic space groups as defined in the International Tables for Crystallography¹⁰¹. An antisymmetry space group is similar to a space group, but some of the symmetry elements may also "flip" space between two possible states, e.g. (r,t) and (r,-t). A double antisymmetry space group extends this

concept to allow symmetry elements to flip space in two independent ways between four possible states, e.g. (r,t,λ) , $(r,-t,\lambda)$, $(r,t,-\lambda)$, and $(r,-t,-\lambda)$. A more precise definition will be given below.

To precisely define antisymmetry space groups, I will start by defining an anti-identity. An operation, e.g. 1', is an anti-identity if it has the following properties:

- Self-inverse: $1' \cdot 1' = 1$ where 1 is identity
- Commutativity: $1' \cdot g = g \cdot 1'$ for all elements g of **E**(3)
- 1' is not an element of **E**(3)

E(3) is the 3-dimensional Euclidean group, *i.e.* the group of all distancepreserving transformations of 3-dimensional Euclidean space. A space group can be defined as a group $G \subset E(3)$ such that the subgroup composed of all translations in G is minimally generated by a set of three translations. We can extend this to define antisymmetry space groups as follows:

Let an *n*-tuple antisymmetry space group be defined as a group $\mathbf{G} \subset \mathbf{E}(3) \times \mathbf{P}$ such that the subgroup composed of all translations in \mathbf{G} is minimally generated by a set of three translations and P is minimally generated by a set of *n* anti-identities and is isomorphic to \mathbb{Z}_2^n .

Thus, for single antisymmetry space groups, **P** is generated by just one antiidentity, for double, two, for triple, three, and so forth. It should be noted that the above definition could be generalized to arbitrary spaces and coloring schemes by changing $\mathbf{E}(3)$ and P respectively, but that is beyond the present scope.

Let the two anti-identities which generate **P** for double antisymmetry space groups be labeled as 1' and 1*. The product of 1' and 1* is also an antiidentity which will be labeled 1'*. The coloring of is intended to assist the reader and has no special meaning beyond that. Double antisymmetry has a total of three anti-identities: 1', 1*, and 1'*. Note that these three anti-identities are not independent because each can be generated from the product of the other two. So although we have three anti-identities, only two are independent and thus we call it "double antisymmetry" (more generally *n*-antisymmetry has 2^{n-1} anti-identities). 1' generates the group 1' = {1, 1'}, 1* generates the group 1* = {1, 1*}, and together 1' and 1* generate the group 1'1* = {1, 1', 1*, 1'*}. For double antisymmetry space groups, P = 1'1*.

Figure 3-1 shows how the elements of $1'1^*$ multiply. To evaluate the product of two elements of $1'1^*$ with the multiplication table given in Figure 3-1a, we find the row associated with the first element and the column associated with second element, e.g. for $1' \cdot 1^*$, go to the second row third column to find $1'^*$. To evaluate the product of two elements of $1'1^*$ with the Cayley graph given in Figure 3-1b, we start from the circle representing the first element and follow the arrow representing the second, e.g. for $1' \cdot 1^*$, we start on the red circle (1') and take the blue path (1*) to the green circle (1'*).



Figure 3-1. Multiplication table and Cayley graph generated by 1', 1*, and 1'*.

a) <u>Multiplication table of 1'1*</u>. To evaluate the product of two elements, we find the row associated with the first element and the column associated with second element, e.g. for 1'·1*, go to the second row third column to find 1*. b) <u>Cayley graph generated by 1', 1*, and 1'*</u>. To evaluate the product of two elements, we start from the circle representing the first element and follow the arrow representing the second, e.g. for 1'·1*, we start on the red circle (1') and take the blue path (1*) to the green circle (1'*).

3.3 The structure of double antisymmetry groups

When a spatial transformation is coupled with an anti-identity, we shall say it is colored with that anti-identity. This is represented by adding ', *, or '* to the end of the symbol representing the spatial transformation, e.g. a four-fold rotation coupled with time-reversal (*i.e.* the product of 4 and 1') is 4'.

All double antisymmetry groups can be constructed by coloring the elements of a colorblind parent group. In the case of a double antisymmetry

space group, the colorblind parent group, **Q**, is one of the crystallographic space groups. There are four different ways of coloring an element of **Q**, namely coloring with 1, 1', 1*, or 1'* which we shall then refer to as being *colorless*, *primed*, *starred*, or *prime-starred* respectively. Let **Q1'1*** be the group formed by including all possible colorings of the elements of **Q**, *i.e.* the direct product of **Q** and **1'1***. Since **Q1'1*** contains all possible colorings of the elements of **Q**, every double antisymmetry space group whose colorblind parent is **Q** must be a subgroup of **Q1'1***. Every subgroup of **Q1'1*** whose colorblind parent is **Q** is of the form of one of the twelve categories of double antisymmetry groups listed in Table 3-1. The formulae of Table 3-1 are represented visually in Section 3.12 using Venn diagrams.

Table 3-1. Double antisymmetry group categories and group structure.

The minus sign, "-", indicates the set-theoretic difference, also known as the relative complement. The plus sign, "+", indicates union. **H** and **K** are unique index-2 subgroups of **Q** (an index-2 subgroup has half as many elements as the group, or equivalently: $|\mathbf{Q}/\mathbf{H}|=2$). These category symbols were introduced by Litvin et al. (1994,1995).

	Symbol o	and	structure	Number of DASG types
(1)	Q	=	Q	230
(2)	Q1'	=	Q + Q]'	230
(3)	Q(H)	=	H + (Q – H)]'	1191
(4)	Q1*	=	Q + Q]*	230
(5)	Q1'1*	=	Q + Q]' + Q]* + Q]'*	230
(6)	Q(H)1*	=	H + (Q-H)]' + H]* + (Q-H)]'*	1191
(7)	Q{H}	=	H + (Q-H)]*	1191
(8)	Q1'*	=	Q + Q]'*	230
(9)	Q{H}1'	=	H + (Q-H)]* + H]' + (Q-H)]'*	1191
(10)	Q(H)1'*	=	H + (Q-H)]' + H]'* + (Q-H)]*	1191
(11)	Q(H){H}	=	H + (Q-H)]'*	1191
(12)	Q(H){K}	=	$H \cap K + (H-K)^{*} + (K-H)^{*} + (Q-(H+K))^{*}$	9507
				Total: 17,803

3.4 Example of generating double antisymmetry groups

As an example, consider applying the formulae in Table 3-1 to point group 222. 222 has four elements: $\{1, 2_x, 2_y, 2_z\}$. 222 has three index-2 subgroups: $\{1, 2_x\}$, $\{1, 2_y\}$, and $\{1, 2_z\}$ which will be denoted by 2_x , 2_y , and 2_z respectively. The subscripts indicate the axes of rotation. Applying the formulae in Table 3-1 yields the following:

Category (1): Q

 $Q = 222 \rightarrow Q = \{1, 2_x, 2_y, 2_z\}$

Category (2): **Q** + **Q**]'

 $Q = 222 \rightarrow Q1' = \{1, 2_x, 2_y, 2_z, 1', 2_x', 2_y', 2_z'\}$

Category (3): H + (Q – H)1'

Q = 222, H = $2_x \rightarrow Q(H) = \{1, 2_x, 2_y', 2_z'\}$ Q = 222, H = $2_y \rightarrow Q(H) = \{1, 2_x', 2_y, 2_z'\}$

 $Q = 222, H = 2_z \rightarrow Q(H) = \{1, 2_x', 2_y', 2_z\}$

Category (4): **Q** + **Q**1*

 $Q = 222 \rightarrow Q1^* = \{1, 2_x, 2_y, 2_z, 1^*, 2_x^*, 2_y^*, 2_z^*\}$

Category (5): Q + Q' + Q* + Q* + Q* + Q*

 $\mathbf{Q} = \mathbf{222} \rightarrow \mathbf{Q1'1*} = \{1, 2_x, 2_y, 2_z, 1', 2_x', 2_y', 2_z', 1^*, 2_x^*, 2_y^*, 2_z^*, 1^{**}, 2_x^{**}, 2_y^{**}, 2_z^{**}\}$

Category (6): H + (Q-H)]' + H]* + (Q-H)]'*

$$Q = 222, H = 2_x \rightarrow Q(H)1^* = \{1, 2_x, 2_y', 2_z', 1^*, 2_x^*, 2_y'^*, 2_z'^*\}$$

$$Q = 222, H = 2_y \rightarrow Q(H)1^* = \{1, 2_x', 2_y, 2_z', 1^*, 2_x'^*, 2_y^*, 2_z'^*\}$$

$$Q = 222, H = 2_z \rightarrow Q(H)1^* = \{1, 2_x', 2_y', 2_z, 1^*, 2_x'^*, 2_y'^*, 2_z^*\}$$

Category (7): **H** + (**Q**-**H**)^{1*}

Q = 222, H =
$$2_x \rightarrow Q\{H\} = \{1, 2_x, 2_y^*, 2_z^*\}$$

Q = 222, H = $2_y \rightarrow Q\{H\} = \{1, 2_x^*, 2_y, 2_z^*\}$
Q = 222, H = $2_z \rightarrow Q\{H\} = \{1, 2_x^*, 2_y^*, 2_z\}$

Category (8): **Q** + **Q**1'*

$$Q = 222 \rightarrow Q1'^{*} = \{1, 2_{x}, 2_{y}, 2_{z}, 1'^{*}, 2_{x}'^{*}, 2_{y}'^{*}, 2_{z}'^{*}\}$$
Category (9): H + (Q-H)1* + H1' + (Q-H)1'*

$$Q = 222, H = 2_{x} \rightarrow Q\{H\}1' = \{1, 2_{x}, 2_{y}^{*}, 2_{z}^{*}, 1', 2_{x}', 2_{y}'^{*}, 2_{z}'^{*}\}$$

$$Q = 222, H = 2_{y} \rightarrow Q\{H\}1' = \{1, 2_{x}^{*}, 2_{y}, 2_{z}^{*}, 1', 2_{x}'^{*}, 2_{y}', 2_{z}'^{*}\}$$

$$Q = 222, H = 2_{z} \rightarrow Q\{H\}1' = \{1, 2_{x}^{*}, 2_{y}^{*}, 2_{z}, 1', 2_{x}'^{*}, 2_{y}'^{*}, 2_{z}'^{*}\}$$

Category (10): H + (Q-H)1' + H1'* + (Q-H)1*

Q = 222, H = $2_x \rightarrow Q(H)1'^* = \{1, 2_x, 2_y', 2_z', 1'^*, 2_x'^*, 2_y^*, 2_z^*\}$ Q = 222, H = $2_y \rightarrow Q(H)1'^* = \{1, 2_x', 2_y, 2_z', 1'^*, 2_x^*, 2_y'^*, 2_z^*\}$

 $\mathbf{Q} = \mathbf{222}, \ \mathbf{H} = \mathbf{2}_{z} \rightarrow \ \mathbf{Q}(\mathbf{H})\mathbf{1'*} = \{1, \mathbf{2}_{x}', \mathbf{2}_{y}', \mathbf{2}_{z}, 1'*, \mathbf{2}_{x}*, \mathbf{2}_{y}*, \mathbf{2}_{z}'*\}$

Category (11): H + (Q-H)1'*

Q = 222, H =
$$2_x \rightarrow Q(H){H} = \{1, 2_x, 2_y'^*, 2_z'^*\}$$

Q = 222, H = $2_y \rightarrow Q(H){H} = \{1, 2_x'^*, 2_y, 2_z'^*\}$

 $Q = 222, H = 2_z \rightarrow Q(H){H} = {1,2_x'^*,2_y'^*,2_z}$

Category (12): H∩K + (H-K) 1* + (K-H) 1' + (Q-(H+K)) 1'*

Q = 222, H = 2_y, K = 2_z
$$\rightarrow$$
 Q(H){K} = {1,2x'*,2y*,2z'}
Q = 222, H = 2_x, K = 2_z \rightarrow Q(H){K} = {1,2x*,2y'*,2z'}
Q = 222, H = 2_x, K = 2_y \rightarrow Q(H){K} = {1,2x*,2y',2z'*}
Q = 222, H = 2_z, K = 2_y \rightarrow Q(H){K} = {1,2x'*,2y',2z*}
Q = 222, H = 2_z, K = 2_x \rightarrow Q(H){K} = {1,2x'*,2y'*,2z*}

$Q = 222, H = 2_y, K = 2_x \rightarrow Q(H)\{K\} = \{1, 2_x', 2_y^*, 2_z'^*\}$

Note that although 29 double antisymmetry point groups are generated from using **222** as a colorblind parent group, they are not all of distinct antisymmetry point group types, as is explained in the next section. In the above example, there are only 12 unique types of groups, as discussed further on. Two additional examples, using point group 2/m and space group Cc, are given in Section 3.13. Since the index-2 subgroups of the crystallographic space groups are already known and available in the International Tables for Crystallography, applying this set of formulae is straightforward. If applied to a representative group of each of the 230 crystallographic space group types, 38,290 double antisymmetry space groups are generated. These 38,290 generated groups can be sorted into 17,803 equivalence classes, *i.e.* double antisymmetry space group types, by applying an equivalence relation.

3.5 Double antisymmetry space group types and the proper affine equivalence relation

The well-known 230 crystallographic space group types given in the International Tables for Crystallography¹⁰¹ are the proper affine classes of space groups ("types" is used instead of "classes" to avoid confusion with "crystal classes"). The equivalence relation of proper affine classes is as follows: two space groups are equivalent if and only if they can be bijectively mapped by a proper affine transformation (proper means chirality-preserving)¹⁰⁰. In the literature, the "space group types" are often referred to as simply "space

groups" when the distinction is unnecessary. "Double antisymmetry space group types" will refer to the proper affine classes of double antisymmetry space groups. This is consistent with Zamorzaev's works on generalized antisymmetry^{110,111,114,115}.

As an example, we will consider the proper affine equivalence classes of the twenty-nine $\mathbf{Q} = 222$ double antisymmetry groups generated using the formulae given in Table 3-1. Only twelve such classes exist, one in each category. For categories (1), (2), (4), (5), and (8), the reason for this is that there is only one group generated in each to begin with. For categories (3), (6), (7), (9), (10), and (11), there are three groups generated which are related to each other by 120 rotations (e.g. {1,2x,2y',2z'} = 3_{xyz} {1,2x',2y',2z} $3_{xyz^{-1}} = 3_{xyz^{-1}}$ {1,2x',2y,2z'} 3_{xyz}) and therefore they are members of the same equivalence class. For category (12), the six generated groups are all in the same equivalence class because {1,2x'*,2y*,2z'} = 3_{xyz} {1,2x*,2y*,2z'*} $3_{xyz^{-1}} = 3_{xyz^{-1}}$ {1,2x*,2y*,2z*} 3_{xyz} = 4_x {1,2x**,2y*,2z*} $4_x^{-1} = 4_x$ 3_{xyz} {1,2x*,2y*,2z**} $3_{xyz^{-1}} = 4_x$ $3_{xyz^{-1}}$ {1,2x*,2y*,2z*} 3_{xyz} 4 x^{-1} . This is demonstrated with point group diagrams in Figure 3-2. Proper affine equivalence and other definitions of equivalence are discussed later in this chapter.




a) through e) show that $\{1, 2_x'^*, 2_y'^*, 2_z'\} = 3_{xyz} \{1, 2_x^*, 2_y', 2_z'^*\} \cdot 3_{xyz^{-1}}$ $= 3_{xyz^{-1}} \cdot \{1, 2_x', 2_y'^*, 2_z^*\} \cdot 3_{xyz}$ $= 4_x \{1, 2_x'^*, 2_y', 2_z^*\} \cdot 4_{x^{-1}}$ $= 4_x \cdot 3_{xyz} \{1, 2_x', 2_y^*, 2_z'^*\} \cdot 3_{xyz^{-1}} \cdot 4_{x^{-1}}$ $= 4_x \cdot 3_{xyz^{-1}} \{1, 2_x^*, 2_y'^*, 2_z'^*\} \cdot 3_{xyz} \cdot 4_{x^{-1}}$

3.6 Derivation of the double antisymmetry space group types

Double antisymmetry space group types of categories (1) through (11) of Table 1-1 are already known or easily derived: The group types of category (1) are the well-known 230 conventional space group types. The groups of categories (2), (4), (5), and (8) are effectively just products of the groups of category (1) with 1', 1*, 1'1*, and 1'* respectively. The groups of category (3) are the well-known black-and-white space groups^{112,113} (also known as type M magnetic space groups¹⁰⁰). The groups of categories (7) and (11) are derived by substituting starred operations and prime-starred operations, respectively, for the primed operations of category (3) groups. And finally, the groups of category (6), (9), and (10) are products of the groups of categories (3), (7), and (11) respectively with 1*, 1', and 1'* respectively.

For the groups of category (12) the following four step procedure was used:

- 1. For one representative group **Q** from each of the 230 types of crystallographic space groups, we list all subgroups of index two^{101,103,105}.
- We construct and list all double antisymmetry space groups Q(H){K} for each representative group Q and pairs of distinct subgroups, H and K, of index two. This step results in 26,052 Q(H){K} groups.
- 3. For every pair of groups Q₁(H₁){K₁} and Q₂(H₂){K₂} where Q₁ and Q₂, H₁ and H₂, and K₁ and K₂, are pair-wise of the same space group type, we evaluate the proper affine equivalence relation to determine if Q₁(H₁){K₁} and Q₂(H₂){K₂} are of the same double antisymmetry space group type.
- 4. From each set of groups belonging to the same type, we list one representative double antisymmetry space group.

Further details for each of these steps are given in later in this chapter.

3.7 Tables of Double Antisymmetry Space Groups

3.7.1 Double antisymmetry space group types

The serial number, symbol, and symmetry operations of a representative aroup of each of the 17,803 double antisymmetry space group types are given in "Double Antisymmetry Space Groups.pdf" of the supplemental materials of the Acta Cryst. paper³⁷ available online А (also at http://sites.psu.edu/gopalan/research/symmetry/ by clicking "Double Antisymmetry Space Groups listing (without diagrams) (35MB)"). The double antisymmetry space group symbols are based on the Hermann-Mauguin symbol of the colorblind parent space group, e.g. C_2^2/m^* is based on C_2/m .

The first part of the symbol gives the lattice centering (or more precisely the translational subgroup). If there are no colored translations in the group, then this part of the symbol is given as *P* (primitive), *C* (*C*-face centered), *A* (A-face centered), *I* (body centered), *F* (all-face centered), or *R* (rhombohedrally centered). If there are colored translations, then *P*, *C*, *A*, *I*, *F*, or *R* is followed by three color operations in parenthesis, e.g. $C(1,1^{*},1^{*})2/m^{*}$. These three color operations denote the coloring of a minimal set of generating lattice translations indicated in Table 3. For example, consider $C(1,1^{*},1^{*})2/m^{*}$: 1 is in the first position, 1'* is in the second position, and 1' is in the third position. Looking up the lattice symbol "C" in the first column of Table 3-2, we find that the first, second, and third positions correspond to $t_{(100)}$, $t_{(001)}$, and $t_{(100)}$, $t_{(001)}^{*}$, and $t_{(200)}^{*}$.

Part of the motivation for labeling the colored translations in this way is that it would generalize to any arbitrary coloring scheme not simply antisymmetry.

Lattice symbol P(1,1,1)	First position <i>P</i> (1 ,1,1)	Second position <i>P</i> (1, 1 ,1)	Third position <i>P</i> (1,1, 1)
Р	†[100]	† _[010]	† _[001]
С	† _[100]	† _[001]	† _[½½0]
А	† _[100]	† _[010]	† _[0½½]
1	t _[100]	† _[001]	† _{[½½½]/2}]
F	† _[0½½]	†[½0½]	†[½½0]
R	† _[001]	$\dagger_{[2/_31/_31/_3]}$	$\dagger_{[\frac{1}{3}^{2}/3^{2}/3]}$

Table 3-2. Coloring of lattice symbols.

The second part of the symbol gives the remaining generators for the double antisymmetry space group. This is also based on the corresponding part of the Hermann-Mauguin symbol of the colorblind parent space group. The Seitz notation of each character is given in "secondPartOfSymbolGenerators.pdf" of the supplemental materials of the Acta Cryst. A paper³⁷ (also available online at: http://sites.psu.edu/gopalan/research/symmetry/).

Finally, if the group is a member of category (2), (4), (5), (6), (8), (9), or (10), then 1', 1^* , $1'1^*$, 1^* , 1', 1'', or 1'* respectively is appended to the end of the symbol.

3.7.2 Using the Computable Document Format (CDF) file

The Computable Document Format (CDF) file, "Double antisymmetry space groups.cdf" provides an interactive way to find the symbols and operations of double antisymmetry space groups. It is given in the supplemental materials of the Acta Cryst. A paper³⁷ (also available online at: http://sites.psu.edu/gopalan/research/symmetry/). The file is opened with the Wolfram CDF Player which can be downloaded from After opening the file, click "Enable http://www.wolfram.com/cdf-player/. Dynamics" if prompted. Provide the necessary input with the drop down menus. A tutorial with screenshots is given in "Double antisymmetry space groups CDF tutorial.pdf".

3.7.3 Using the PDF file

In the PDF file, "Double Antisymmetry Space Groups.pdf", the 17,803 double antisymmetry space groups are listed sequentially in Seitz notation. The first portion of the file contains links to each group entry. These links are sorted by the colorblind parent group, e.g. C^2/m^* is listed under the space group number of C^2/m (i.e. 'SG. 12') as "8543. C^2/m^* ". Clicking on the "8543. C^2/m^* " link will bring you to C^2/m^* 's listing as shown in Figure 3-3.

No. 8543 SG. 12	$\frac{C2'}{m^*}$ 2'/m*		C2 Monoclinic		
Symmetry Operations					
For (0,0,0)+ set (1) 1 (1 000)	(2) $2' 0, y, 0$ $(2_y 000)'$	(3)	$ar{1}'^* 0, 0, 0 \ (ar{1} 000)'^*$	(4) $m^* x, 0, z$ $(m_y 000)^*$
For $(\frac{1}{2}, \frac{1}{2}, 0) + $ set (1) $t(\frac{1}{2}, \frac{1}{2}, 0)$ $(1 \frac{1}{2}, \frac{1}{2}, 0)$	(2) $2(0,\frac{1}{2},0)' (2_y \frac{1}{2}\frac{1}{2}\frac{1}{2}0)'$	$\frac{1}{4}, y, 0$ (3)	$ \frac{\bar{1}'^*}{(\bar{1} \frac{1}{2},\frac{1}{2},0)} (\bar{1} \frac{1}{2},\frac{1}{2},0)'^* $	(4)) $a^* x, \frac{1}{4}, z$ $(m_y \frac{1}{2} \frac{1}{2} 0)^*$

Figure 3-3. No. 8543 C²/*m*^{*}, listing in "Double Antisymmetry Space Groups.pdf".

The first line of each entry gives the sequential serial number (1 through 17,803), the double antisymmetry space group symbol and the "X-ray diffraction symmetry group" (*i.e.* the symmetry group obtained by removing all of the starred and prime-starred operations and changing all of the primed operations to colorless operations). The second line gives the number of the colorblind parent group, the double antisymmetry point group and the crystal system. The remaining lines give the symmetry operations of the group: a set of coset representatives of the group with respect to the translational subgroup generated by translations of the conventional unit cell. These symmetry operations are given in International Tables Volume A notation and Seitz notation.

"X-ray diffraction symmetry group" (*Cm* in Figure 3-3) is a somewhat misleading name that I came up with when our purpose for listing the double antisymmetry space groups was to apply it to rotation-reversal symmetry. It was meant to be the symmetry one would expect to find for a crystal using conventional X-ray diffraction techniques that are insensitive to spin polarization. Although the description as " the symmetry group obtained by removing all of

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the starred and prime-starred operations and changing all of the primed operations to colorless operations" is accurate, problems with rotation-reversal symmetry implementation (see Chapter 4) interfered with the application of this concept. In my opinion, there is also a problem for the magnetic symmetry aspects of this "X-ray diffraction symmetry group". For many magnetic crystals, it is common for the underlying atomic structure (the paramagnetic parent structure) to be classified with a higher symmetry than would be achieved by converting the time-reversed operations to colorless operations (i.e. the colorblind parent). For example, ferromagnetic iron with a magnetic moment along [001] is often characterized as having $Im\bar{3}m$ symmetry and indeed X-ray diffraction methods cannot resolve any difference in lattice spacing for (100), (010), and (001), despite the fact that the cubic symmetry is clearly broken by the magnetic moment. The magnetic symmetry of ferromagnetic iron with a magnetic moment along [001] is I4/mm'm' and so the colorblind parent group is 14/mmm. Thus, with this example, the "X-ray diffraction symmetry group" 14/mmm is not what would be found by conventional X-ray diffraction methods but a subgroup of it (14/mmm is an index-3 subgroup of $Im\overline{3}m$). This kind of situation where the atomic structure appears to have more symmetry than the magnetic is common and may be due to relatively weak spin-lattice coupling, i.e. the magnetic moments of atoms might not strongly influence their atomic positions.

Two additional examples from "Double Antisymmetry Space Groups.pdf" are given in Figure 3-5 and Figure 3-6.

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Figure 3-4. No. 16490 *I*4*/*mm*[']*m*^{'*} listing in "Double Antisymmetry Space Groups.pdf".



Figure 3-5. No. 13461 Ib'*c'a' listing in "Double Antisymmetry Space Groups.pdf".

3.7.4 Machine-readable file

A "machine-readable" file, "DASGMachineReadable.txt" is intended to provide a simple way to use the double antisymmetry space groups in code or software such as MatLab or Mathematica. The structure of the file is given in the file called "Using the Machine Readable File.pdf". The file, "Import DASGMachineReadable.nb" has been provided to facilitate loading into Mathematica. These files are given in the supplemental materials of our Acta this work³⁷ available Cryst. А article on (also online at: http://sites.psu.edu/gopalan/research/symmetry/).

3.7.5 Symmetry Diagrams

In Figure 3-6, Figure 3-7, and Figure 3-8, symmetry diagrams have been made for the example double antisymmetry space groups listed in Figure 3-3, Figure 3-4, and Figure 3-5. These diagrams are intended to extend the conventional space group diagrams such as those in the International Tables for Crystallography.

In Figure 3-6, double antisymmetry space group No. 8543, $C2'/m^*$, is projected along the *b*-axis. The red lenticular shape with the green dot inset, *i.e.*

, indicates the position of a primed two-fold rotation axis (2') and a primestarred point of inversion ($\overline{1}$) coinciding with the plane of projection. Likewise, the lenticular shapes with "tails", *i.e.* , indicate screw axes. The same symbols but with a " $\frac{1}{4}$ " placed near the upper left corner indicate that the prime-starred point of inversion is out-plane by a displacement of $\frac{1}{4}$ along the *b*-

axis. The $\int_{-}^{-} \frac{1}{4}$ on the bottom left of the diagram indicates that there is a starred mirror (m*) coinciding with the plane of projection and a starred glide plane (a*) out-plane by a displacement of $\frac{1}{4}$ along the *b*-axis.

In Figure 3-7, double antisymmetry space group No. 16490, *I4*/mm'm'**, is projected along the c-axis. In Figure 3-8, double antisymmetry space group No. 13461, *Ib'*c'a'*, is projected along the c-axis. As with Figure 3-6, the symbols in these diagrams are naturally extended from those used for conventional space groups in the International Tables for Crystallography.



Figure 3-6. No. 8543 C_2^{\prime}/m^* symmetry diagram.



Figure 3-7. No. 16490 I4*/mm'm'* symmetry diagram.



Figure 3-8. No. 13461 *Ib*'*c'a' symmetry diagram.

3.7.6 Computation Details

The majority of the computation was performed in Mathematica using 4x4 augmented matrices to represent space group operations and unit-cell transformations (more generally, affine transformations). The use of augmented matrices to represent space group operations and unit-cell transformations is described in the International Tables for Crystallography and in the rest of this chapter. These matrices were downloaded for each space group type from the GENPOS tool on Bilbao Crystallographic Server, http://www.cryst.ehu.es/cryst/get_gen.html ¹⁰³⁻¹⁰⁵. The standard setting was used for each of the 230 space group types as given in the International Tables for Crystallography.

3.8 Augmented matrices

Every space group operation can be broken up into a linear transformation R and a translation t which transform the coordinates (r_1, r_2, r_3) into (r_1', r_2', r_3') :

 $\mathbf{r}' = \mathbf{R}\mathbf{r} + \mathbf{t}$

$$\begin{pmatrix} r_1' \\ r_2' \\ r_3' \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} \\ R_{21} & R_{22} & R_{23} \\ R_{31} & R_{32} & R_{33} \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \end{pmatrix} + \begin{pmatrix} t_1 \\ t_2 \\ t_3 \end{pmatrix}$$

It is convenient to condense this linear transformation and translation into a single square matrix called an augmented matrix:

$$\begin{pmatrix} r_1' \\ r_2' \\ r_3' \\ 1 \end{pmatrix} = \begin{pmatrix} R_{11} & R_{12} & R_{13} & t_1 \\ R_{21} & R_{22} & R_{23} & t_2 \\ R_{31} & R_{32} & R_{33} & t_3 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ 1 \end{pmatrix}$$

Note that the final row is necessary to make a square 4x4 matrix but contains no information specific to the transformation. When using these augmented matrices to represent space group operations, the product of two space group operations is evaluated by matrix multiplication, *i.e.* g_1g_2 is performed by multiplying the matrices which represent g_1 and g_2 to get a product matrix which is also an augmented matrix that represents a space group operation. The inverse of a space group operation is represented by the matrix inverse of the operation's augmented matrix. The sign of the determinant of an augmented matrix representing a space group operation determines if it is proper. A positive determinant means that it is proper (orientation-preserving).

For a set of 4x4 matrices **S** and a 4x4 matrix A, the set formed by conjugating of each element of **S** by A will be denoted as ASA^{-1} , *i.e.* $ASA^{-1} = {ASA^{-1}: s \in S}$.

3.9 Index-2 subgroups

To evaluate the formulae in Table 3-1 for any given colorblind parent space group \mathbf{Q} , the index-2 subgroups of \mathbf{Q} are needed. The index-2 subgroups of a space group are also space groups themselves. As such, every index-2 subgroup of space group \mathbf{Q} must be one of the 230 types of space groups. Using this, we can specify an index-2 subgroup of **Q** by specifying the type of the subgroup (1 to 230) and a transformation from a standard representative group of that type. This is to say that **H**, a subgroup of **Q**, can be specified by a standard representative group H_0 and the transformation, *T* such that $H = TH_0T^{-1}$. Note this is just the usual linear algebra change of basis formula; we are simply using *T* to transform from the standard conventional basis to the basis which makes **H** a subgroup of **Q**.

Q, **H**, and **H**₀ are each represented by a set of 4x4 real matrices. *T* is represented by a single 4x4 real matrix. For every element *h* in **H** there is an element h_0 in **H**₀ such that $h = Th_0T^{-1}$. Thus, we make the set of matrices representing **H** by computing Th_0T^{-1} for each matrix in the set representing **H**₀.

The index-2 subgroup data was downloaded from the Bilbao Crystallographic Server. All together there are 1,848 index-2 subgroups among the 230 representative space groups. Each entry (out of 1,848) consisted of: a number between 1 and 230 for the space group type of \mathbf{Q} , a number between 1 and 230 for the space group type of \mathbf{T} .

3.10 Normalizer method for evaluating the proper affine equivalence of Q(H){K} groups

The proper affine equivalence relation can be defined as: two groups, G_1 and G_2 , are equivalent if and only if G_1 can be bijectively mapped to G_2 by a proper affine transformation, *a*. Expressed in mathematical short-hand, this is:

$$\mathbf{G}_2 \sim \mathbf{G}_1 \equiv \exists a \in \mathcal{A}^+ : (\mathbf{G}_2 = a\mathbf{G}_1 a^{-1})$$

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where ~ is the proper affine equivalence relational operator, \equiv is logical equivalence ("is logically equivalent to"), $\exists a$ is the existential quantification of a ("there exists a"), \in means "an element of", : means "such that", and \mathcal{A}^+ is the group of proper affine transformations. An affine transformation is the combination of a linear transformation and a translation. A proper affine transformation that is orientation-preserving (*i.e.* preserves chirality).

For evaluating the proper affine equivalence of a pair of **Q(H){K}** groups, if the space group types of **Q**, **H**, and **K** of one of the **Q(H){K}** groups are not the same as those of the other, then the proper affine equivalence relation fails and no further work is necessary. For a pair of **Q(H){K}** groups where they are the same, I have derived a method to evaluate proper affine equivalence based on affine normalizers. To begin this derivation, we can expand the proper affine equivalence for **Q(H){K}** groups to:

 $Q(H_2){K_2} \sim Q(H_1){K_1} \equiv \exists a \in \mathcal{A}^+ : (Q = aQa^{-1}) \land (H_2 = aH_1a^{-1}) \land (K_2 = aK_1a^{-1})$ where \land denotes logical conjuction ("and"). The subscripts have been omitted for Q_1 and Q_2 because we are testing the equivalence of $Q(H){K}$ groups where $Q_1 = Q_2$. We can use the definition of the proper affine normalizer group¹⁰⁰ of Q, *i.e.* $N_{\mathcal{A}^+}(Q) = \{a \in \mathcal{A}^+ : Q = aQa^{-1}\}$ iv to get:

$$\mathbf{Q}(\mathbf{H}_2)\{\mathbf{K}_2\} \sim \mathbf{Q}(\mathbf{H}_1)\{\mathbf{K}_1\} \equiv \exists a \in \mathbf{N}_{\mathcal{A}^+}(\mathbf{Q}) : (\mathbf{H}_2 = a\mathbf{H}_1a^{-1}) \land (\mathbf{K}_2 = a\mathbf{K}_1a^{-1})$$

^{iv} If **Q** contains improper motions, then $\mathbf{N}_{\mathcal{A}^+}(\mathbf{Q})$ is not actually a normalizer group because $\mathbf{Q} \not\subset \mathcal{A}^+$. In these cases, $\mathbf{N}_{\mathcal{A}^+}(\mathbf{Q})$ can be interpreted as $\mathbf{N}_{\mathcal{A}}(\mathbf{Q}) \cap \mathcal{A}^+$. This does not affect the results.

H₁ and H₂ are mapped by proper affine transformations, T_{H_1} and T_{H_2} respectively, from a standard representative group, H₀, as follows: H₁ = $T_{H_1}H_0T_{H_1}^{-1}$ and H₂ = $T_{H_2}H_0T_{H_2}^{-1}$. Likewise, K₁ and K₂ are mapped by proper affine transformations, T_{K_1} and T_{K_2} respectively, from a standard representative group, K₀, as follows: K₁ = $T_{K_1}K_0T_{K_1}^{-1}$ and K₂ = $T_{K_2}K_0T_{K_2}^{-1}$. Thus, by substitution, (H₂ = aH_1a^{-1}) \wedge (K₂ = aK_1a^{-1}) is equivalent to $(T_{H_2}H_0T_{H_2}^{-1} = aT_{H_1}H_0T_{H_1}^{-1}a^{-1}) \wedge$ $(T_{K_2}K_0T_{K_2}^{-1} = aT_{K_1}K_0T_{K_1}^{-1}a^{-1})$ which can be rearranged to $(H_0 = (T_{H_2}^{-1}aT_{H_1})H_0(T_{H_2}^{-1}aT_{H_1})^{-1}) \wedge (K_0 = (T_{K_2}^{-1}aT_{K_1})K_0(T_{K_2}^{-1}aT_{K_1})^{-1})$. By applying the definition of a normalizer group again, we find that $T_{H_2}^{-1}aT_{H_1} \in$ $N_{\mathcal{A}^+}(H_0)$ and $T_{K_2}^{-1}aT_{K_1} \in N_{\mathcal{A}^+}(K_0)$, which rearrange to $a \in T_{H_2}N_{\mathcal{A}^+}(H_0)T_{H_1}^{-1}$ and $a \in T_{K_2}N_{\mathcal{A}^+}(K_0)T_{K_1}^{-1}$ respectively. Therefore, the proper affine equivalence of Q(H₁){K₁} and Q(H₂){K₂} is logically equivalent to the existence of a non-empty

intersection of $\mathbf{N}_{\mathcal{A}^+}(\mathbf{Q})$, $T_{H_2}\mathbf{N}_{\mathcal{A}^+}(\mathbf{H}_0)T_{H_1}^{-1}$, and $T_{K_2}\mathbf{N}_{\mathcal{A}^+}(\mathbf{K}_0)T_{K_1}^{-1}$:

 $\mathbf{Q}(\mathbf{H_1})\{\mathbf{K_1}\} \sim \mathbf{Q}(\mathbf{H_2})\{\mathbf{K_2}\} \equiv \mathbf{N}_{\mathcal{A}^+}(\mathbf{Q}) \cap T_{H_2}\mathbf{N}_{\mathcal{A}^+}(\mathbf{H_0})T_{H_1}^{-1} \cap T_{K_2}\mathbf{N}_{\mathcal{A}^+}(\mathbf{K_0})T_{K_1}^{-1} \neq \emptyset$

This simplifies the problem of evaluating the equivalence relation to either proving that the intersection has at least one member or proving that it does not. To do this, I applied Mathematica's built-in "FindInstance" function. As with the subgroup data, the normalizer group data was downloaded from the Bilbao Crystallographic Server. As previously discussed, the formulae in Table 3-1 generate 38,290 double antisymmetry space groups when applied to all 230 representative space groups. With the aid of Mathematica, these 38,290 double antisymmetry space groups were partitioned by the equivalence relation given above into 17,803 proper affine equivalence classes, *i.e.* 17,803 double antisymmetry space group types.

This method can be easily generalized to other types of antisymmetry and color symmetry. For example, for antisymmetry groups formed from one index-2 subgroup, such as **Q(H)** groups, the condition simply reduces to the following:

$$\mathbf{Q}(\mathbf{H}_1) \sim \mathbf{Q}(\mathbf{H}_2) \equiv \mathbf{N}_{\mathcal{A}^+}(\mathbf{Q}) \cap T_{H_2} \mathbf{N}_{\mathcal{A}^+}(\mathbf{H}_0) T_{H_1}^{-1} \neq \emptyset$$

For finding the double antisymmetry space group types, only conditions for Q(H) and $Q(H){K}$ groups are necessary. This is because it is trivial to map these results to all the other categories of double antisymmetry space groups. This normalizer method is demonstrated later in this chapter to derive all double antisymmetry space group types where Q = Cc.

3.11 Number of Types of Double Antisymmetry Space Groups

The total number of types of double antisymmetry space groups listed by the present work is 17,803. The total number of $Q(H){K}$ types this listed by the present work is 9,507. These values differ from those given by Zamorzaev & Palistrant¹¹⁰. We have found four fewer $Q(H){K}$ types where Q = lbca (#73 on the International Tables for Crystallography). Since there are only a small number of discrepancies between our listing and the numbers calculated by Zamorzaev & Palistrant, each will be addressed explicitly. Zamorzaev & Palistrant gave a list of double antisymmetry space group generators in noncoordinate notation¹²⁴. For Ibca (21a in Zamorzaev & Palistrant) the following generators are used:

$$\left\{a, b, \frac{a+b+c}{2}\right\} \left(\frac{c}{2} 2 \cdot \frac{b}{2} m : \frac{a}{2} 2_{\frac{b}{4}}\right)$$

a, *b*, $\frac{a+b+c}{2}$, $\frac{c}{2}2$, $\frac{b}{2}m$, and $\frac{a}{2}2_{\frac{b}{4}}$ can be interpreted, in Seitz notation, as (1 | 100), (1 | $\frac{1}{2}\frac{1}{2}\frac{1}{2}$), (2_z | $\frac{1}{2}0\frac{1}{2}$), (m_x | $\frac{1}{2}\frac{1}{2}0$), and (2_x | $\frac{1}{2}\frac{1}{2}0$) respectively.

Zamorzaev & Palistrant couple these generators with anti-identities to give generating sets for double antisymmetry space groups. However, unlike the more explicit listing given in the present work, Zamorzaev & Palistrant give only generating sets and only those which are unique under the permutations of the elements of 1'1* that preserve the group structure, i.e. the automorphisms of 1'1*. Because of this concise method of listing generating sets (only 1846 Q(H){K} generating sets are necessary), a single generating set given by Zamorzaev & Palistrant can represent up to six types under the proper affine equivalence relation. The six possible types correspond to the six automorphisms of 1'1*.

The automorphisms of **1'1*** correspond to the possible permutations of the three anti-identities of double antisymmetry: $(1', 1^*, 1'^*)$, $(1', 1'^*, 1^*)$, $(1^*, 1', 1'^*)$, $(1^*, 1', 1'^*)$, $(1^*, 1', 1'^*)$, $(1^*, 1', 1^*)$, $(1^*, 1^*, 1^*)$, and $(1^{1*}, 1^*, 1^*)$, *i.e.* Aut $(1'1^*) \cong S_3$. Zamorzaev & Palistrant give the number of types represented by each line, but not which automorphisms must be applied to get them. This is discussed in the supplemental materials file called "Color Automorphisms of Double Antisymmetry.pdf". There are only two

lines of generators from Zamorzaev & Palistrant for which their resulting number of **Q(H){K**} types differs from this work. These lines are given in Table 3-3.

Applying the six automorphisms of **1'1*** to lbc'a'* from the first line of Table 3-3, we get lbc'a'*, lbc'a*, lbc*a'*, lbc*a', lbc*a*, and lbc'*a'. According Zamorzaev & Palistrant, these are six distinct types whereas there are actually only three distinct types. Ibc'a'* and lbc'*a' are of type No. 13460. Ibc'a* and lbc*a' are of type No. 13462. Ibc*a'* and lbc'*a* are of type No.13450. Applying the six automorphisms of **1'1*** to lb*c'*a' from the second line of Table 3-3, we get lb*c'*a', lb'*c*a', lb'*c'a*, lb'c*a'*, and lb*c'a'*. According Zamorzaev & Palistrant, these correspond to two distinct types whereas they are actually all the same type, No. 13447.

Consequently, the generators in the first line of Table 3-3 map to three types and the generators in the second line map to one type, not six and two respectively. Thus, there are four fewer **Q(H){K}** types than the number given by Zamorzaev & Palistrant, *i.e.* 9507 rather than 9511. This error likely affects the number of higher order multiple antisymmetry groups calculated by Zamorzaev & Palistrant, as well. We conjecture that there are 24 fewer non-trivial triple antisymmetry space groups then calculated by Zamorzaev & Palistrant but that the numbers for other multiple antisymmetries are correct. If we are correct, this would mean that the number in the final column of Table 1 of "Generalized Antisymmetry" by Zamorzaev¹¹¹ should read 230, 1191, <u>9507</u>, <u>109115</u>, 1640955, 28331520, and 419973120, rather than 230, 1191, <u>9511</u>, <u>109139</u>, 1640955, 28331520, and 419973120 (the numbers which differ are <u>underlined</u>). Similarly, if we are

correct, the final column of Table 2 of the same work should read 230, 1651,

17803, 287574, 6879260, 240768842, and 12209789596 rather than 230, 1651,

17807, 287658, 6880800, 240800462 (typo'ed as 240900462), and 12210589024.

The results shown in this chapter also confirm that there are 5005 types of

Q(H){K} Mackay groups^{120,121,123}.

Table 3-3. Comparison with double antisymmetry space group generating sets listed by Zamorzaev & Palistrant¹¹⁰.

The numbers in the second and third columns refer to the number of unique types obtained by the permutation of anti-identities.

Generating line from Zamorzaev & Palistrant	Symbol in present work	# of types (Zamorzaev & Palistrant)	Actual number (present work)	Difference
$\left\{a, b, \frac{a+b+c}{2}\right\} \left(\frac{c}{2} 2' \cdot \frac{b}{2} m: \frac{a}{2} 2\frac{b}{\frac{b}{4}}\right)$	lbc'a'*	6	3	-3
$\left\{a, b, \frac{a+b+c}{2}\right\} \left(\frac{c}{2} \mathbf{2'} \cdot \frac{b}{2} m^* : \frac{a}{2} 2_{\frac{b}{4}}^*\right)$	lb*c'*a'	2	1	-1

3.12 Visual representation of DASG category structures using Venn diagrams

Table 3-4 gives a visual representation of double antisymmetry space group (DASG) category structures. In the table, the set of operations in a group



and **Q**1'*= **C**. Following this scheme, the twelve categories of double antisymmetry groups can be represented as shown in Table 3-4. These category symbols, e.g. **Q(H){K}**, were introduced by Litvin et al.^{125,126}. They are intended as a generalization of the widely used **Q(H)** notation for magnetic groups. The "()" brackets enclose a subset which is not primed. The "{}" brackets enclose a subset which is not primed. The "{}" brackets enclose a subset which is not primed. The "{}" brackets enclose a that 1', 1*, 1'*, or 1' 1*, 1'*, or 1' 1* at the end of a symbol indicates that 1', 1*, 1'*, or 1' and 1*, respectively, are elements of the group.

Category	Category Symbol		Category Structure
(1)	Q	Π	Q
(2)	Q1'	Ш	Q + Q]'
	+	=	+ 1'
(3)	Q(H)	=	H + (Q – H) 1'
		=	+ 1'
(4)	Q1*	Ш	Q + Q]*
	+	Π	+ 1*
(5)	Q1'1*	=	Q + Q' + Q' + Q' + Q''
	+ + + +	=	+ 1'+ 1*+ 1'*
(6)	Q(H)1*	Ш	H + (Q-H)]' + H]* + (Q-H)]'*
	+	II	+ 1'+ 1*+ 1'*
(7)	Q{H}	Ш	H + (Q-H)]*
		=	+ 1*
(8)	Q1'*	Ш	Q + Q] ¹ *
	+	=	+ 1'*
(9)	Q{H}1'	Ш	H + (Q-H)]* + H]' + (Q-H)]'*
	+	=	+ 1*+ 1' + 1'*
(10)	Q(H)1'*	Ш	H + (Q-H)]' + H]'* + (Q-H)]*
	+	=	+ 1'+ 1'*+ 1*
(11)	Q(H){H}	=	H + (Q-H)]'*
		=	+ 1'*
(12)	Q(H){K}	=	H∩K + (H-K)]* + (K-H)]' + (Q-(H+K))]'*
		=	+ 1*+ 1' + 1'*

Table 3-4. Visual representation of DASG category structures using Venn diagrams.

3.13 Additional examples of generating double antisymmetry groups

2/m has four elements: {1,2,m,-1}. 2/m has three index-2 subgroups: {1,2},
{1,m}, and {1,-1} which will be referred to as 2, m, and -1 respectively.

Category (1): Q

 $Q = 2/m \rightarrow Q = \{1, 2, m, -1\}$

Category (2): Q + Q1'

 $Q = 2/m \rightarrow Q1' = \{1, 2, m, -1, 1', 2', m', -1'\}$

Category (3): H + (Q – H)1'

 $Q = 2/m, H = 2 \rightarrow Q(H) = \{1, 2, m', -1'\}$

 $Q = 2/m, H = m \rightarrow Q(H) = \{1, 2', m, -1'\}$

 $Q = 2/m, H = -1 \rightarrow Q(H) = \{1, 2', m', -1\}$

Category (4): **Q** + **Q**1*

 $Q = 2/m \rightarrow Q1^* = \{1, 2, m, -1, 1^*, 2^*, m^*, -1^*\}$

Category (5): Q + Q]' + Q]* + Q]'*

$$Q = 2/m \rightarrow Q1'1^* = \{1, 2, m, -1, 1', 2', m', -1', 1^*, 2^*, m^*, -1^*, 1^*, 2^{**}, m^{**}, -1^{**}\}$$

Category (6): **H** + (**Q**-**H**)]' + **H**]* + (**Q**-**H**)]'*

$$Q = 2/m, H = 2 \rightarrow Q(H)1^* = \{1, 2, m', -1', 1^*, 2^*, m'^*, -1'^*\}$$
$$Q = 2/m, H = m \rightarrow Q(H)1^* = \{1, 2', m, -1', 1^*, 2'^*, m^*, -1'^*\}$$
$$Q = 2/m, H = -1 \rightarrow Q(H)1^* = \{1, 2', m', -1, 1^*, 2'^*, m'^*, -1^*\}$$

Category (7): H + (Q-H)1*

Q = 2/m, H = 2
$$\rightarrow$$
 Q{H} = {1,2,m*,-1*}
Q = 2/m, H = m \rightarrow Q{H} = {1,2*,m,-1*}
Q = 2/m, H = -1 \rightarrow Q{H} = {1,2*,m*,-1}

Category (8): **Q** + **Q**1'*

$$Q = 2/m \rightarrow Q1'* = \{1, 2, m, -1, 1'*, 2'*, m'*, -1'*\}$$

Category (9): H + (Q-H)1* + H1' + (Q-H)1'*

$$Q = 2/m, H = 2 \rightarrow Q\{H\}1' = \{1, 2, m^*, -1^*, 1', 2', m^{'*}, -1^{'*}\}$$
$$Q = 2/m, H = m \rightarrow Q(H\}1' = \{1, 2^*, m^*, -1^{**}\}$$

$$Q = 2/m, n = m \rightarrow Q(n) = \{1, 2^{\circ}, (1), -1^{\circ}, 1, 2^{\circ}, (1), -1^{\circ}\}$$

$$Q = 2/m, H = -1 \rightarrow Q{H}1' = {1,2^*,m^*,-1,1',2^*,m^*,-1'}$$

Category (10): H + (Q-H)]' + H]'* + (Q-H)]*

$$Q = 2/m, H = 2 \rightarrow Q(H)1'* = \{1,2,m',-1',1'*,2'*,m^*,-1^*\}$$
$$Q = 2/m, H = m \rightarrow Q(H)1'* = \{1,2',m,-1',1'*,2^*,m^{*},-1^*\}$$
$$Q = 2/m, H = -1 \rightarrow Q(H)1'* = \{1,2',m',-1,1'*,2^*,m^*,-1^{**}\}$$

Category (11): H + (Q-H)1'*

Q = 2/m, H = 2
$$\rightarrow$$
 Q(H){H} = {1,2,m'*,-1'*}
Q = 2/m, H = m \rightarrow Q(H){H} = {1,2'*,m,-1'*}
Q = 2/m, H = -1 \rightarrow Q(H){H} = {1,2'*,m'*,-1}

Category (12): $H \cap K + (H-K)$ + (K-H) + (Q-(H+K))

$$Q = 2/m, H = m, K = -1 \rightarrow Q(H)\{K\} = \{1, 2^{1*}, m^{*}, -1^{1}\}$$

$$Q = 2/m, H = 2, K = -1 \rightarrow Q(H)\{K\} = \{1, 2^{*}, m^{1*}, -1^{1}\}$$

$$Q = 2/m, H = 2, K = m \rightarrow Q(H)\{K\} = \{1, 2^{*}, m^{1}, -1^{1*}\}$$

$$Q = 2/m, H = -1, K = m \rightarrow Q(H)\{K\} = \{1, 2^{1*}, m^{1}, -1^{*}\}$$

$$Q = 2/m, H = -1, K = 2 \rightarrow Q(H)\{K\} = \{1, 2^{1*}, m^{1*}, -1^{*}\}$$

$$Q = 2/m, H = m, K = 2 \rightarrow Q(H)\{K\} = \{1, 2^{1*}, m^{1*}, -1^{1*}\}$$

Both **2/m** and **222** (given as an example in Section 3.4) have three index-2 subgroups. Consequently, they generate the same number of double

antisymmetry groups: 29. However, unlike with **222**, none of the 29 groups formed from **2/m** are in the same equivalence class. This may seem surprising given that **2/m** is isomorphic to **222**. This can be thought of as being a consequence of the fact that none of the elements of **2/m** can be rotated into one another whereas the three two-fold axes of **222** can. Another way to look at it is to consider that the subgroup of proper rotations of **2/m**'s affine normalizer group (**~22**) does not contain non-trivial automorphisms of whereas that of **222** (**432**).

As with all crystallographic space groups, Cc has an infinite number of elements due to the infinite translational subgroup. Cc's elements will be represented as $(t_{[100]},t_{[001]},t_{[1/2/20]})$ (1,c} where $(t_{[100]},t_{[001]},t_{[1/2/20]})$ represent the generators of the translation subgroup and (1,c) are coset representatives of the corresponding decomposition. Cc has three index-2 subgroups: $(t_{[100]},t_{[001]},t_{[1/2/20]})$ (1,c}, and $(t_{[100]},t_{[001]})$ (1, $t_{[1/2/20]}$ ·c}.

Category (1): Q

 $\mathbf{Q} = CC \rightarrow \mathbf{Q} = (t_{100}, t_{001}, t_{\frac{1}{2}}) \{1, C\}$

Category (2): Q + Q1'

 $\mathbf{Q} = CC \rightarrow \mathbf{Q1'} = (t_{[100]}, t_{[001]}, t_{[\frac{1}{2}\frac{1}{2}0]})\{1, C, 1', C'\}$

Category (3): H + (Q - H)1'

 $\mathbf{Q} = CC, \ \mathbf{H} = (t_{[100]}, t_{[001]}, t_{[\frac{1}{2}\frac{1}{2}0]})\{1\} \rightarrow \mathbf{Q}(\mathbf{H}) = (t_{[100]}, t_{[001]}, t_{\frac{1}{2}\frac{1}{2}\frac{1}{2}0})\{1, \mathbf{C}'\}$

 $\mathbf{Q} = CC, \ \mathbf{H} = (t_{[100]}, t_{[010]}, t_{[001]}) \{1, C\} \rightarrow \mathbf{Q}(\mathbf{H}) = (t_{[100]}, t_{[001]}, t_{[122]}) \{1, C\}$

 $\mathbf{Q} = CC, \ \mathbf{H} = (t_{[100]}, t_{[001]}, t_{[001]}) \{1, t_{[1/2]/20]} \cdot C\} \rightarrow \mathbf{Q}(\mathbf{H}) = (t_{[100]}, t_{[001]}, t_{[1/2]/20]}) \{1, C'\}$

Category (4): **Q** + **Q**1*

 $\mathbf{Q} = CC \rightarrow \mathbf{Q1*} = (\dagger_{[100]}, \dagger_{[001]}, \dagger_{[1/2^{1/2}0]}) \{1, C, 1^{*}, C^{*}\}$

Category (5): **Q** + **Q**]' + **Q**]* + **Q**]'*

 $\mathbf{Q} = \mathbf{C}\mathbf{C} \rightarrow \mathbf{Q1'1*} = (\dagger_{[100]}, \dagger_{[001]}, \dagger_{[\frac{1}{2}\frac{1}{2}0]})\{1, \mathbf{C}, \frac{1}{\mathbf{C}}, \frac{1}$

Category (6): H + (Q-H)1' + H1* + (Q-H)1'*

 $\mathbf{Q} = \mathbf{C}\mathbf{C}, \ \mathbf{H} = (t_{[100]}, t_{[001]}, t_{[1/2/20]})\{1\} \rightarrow \mathbf{Q}(\mathbf{H})\mathbf{1}^* = (t_{[100]}, t_{[001]}, t_{[1/2/20]})\{1, \mathbf{C}', 1^*, \mathbf{C}'^*\}$

 $\mathbf{Q} = CC, \mathbf{H} = (t_{100]}, t_{001]}, t_{001]}, t_{1,C} \rightarrow \mathbf{Q}(\mathbf{H})\mathbf{1}^* = (t_{100]}, t_{001]}, t_{1/2/20}')\{1, C, 1^*, C^*\}$

 $\mathbf{Q} = \mathbf{Cc}, \, \mathbf{H} = (\mathbf{1}_{[100]}, \mathbf{1}_{[010]}, \mathbf{1}_{[001]}) \{\mathbf{1}, \mathbf{1}_{[\frac{1}{2}\frac{1}{2}0]} \cdot \mathbf{C}\} \rightarrow \mathbf{Q}(\mathbf{H}) \mathbf{1}^* =$

(†[100],†[001],†[½½0]'){1,C',1*,C'*}

Category (7): **H** + (**Q**-**H**)1*

 $\mathbf{Q} = \mathbf{C}\mathbf{C}, \ \mathbf{H} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[1/2/20]})\{1\} \rightarrow \mathbf{Q}\{\mathbf{H}\} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[1/2/20]})\{1, \mathbb{C}^*\}$

 $\mathbf{Q} = CC, \ \mathbf{H} = (t_{[100]}, t_{[010]}, t_{[001]}) \{1, C\} \rightarrow \mathbf{Q} \{\mathbf{H}\} = (t_{[100]}, t_{[001]}, t_{[1/2/20]}^*) \{1, C\}$

 $\mathbf{Q} = \mathbf{C}\mathbf{C}, \ \mathbf{H} = (\mathsf{t}_{[100]}, \mathsf{t}_{[010]}, \mathsf{t}_{[001]})\{1, \mathsf{t}_{[1/2/20]} \cdot \mathbf{C}\} \rightarrow \mathbf{Q}\{\mathbf{H}\} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[1/2/20]} *)\{1, \mathbf{C}^*\}$

Category (8): **Q** + **Q**1'*

 $\mathbf{Q} = \mathbf{C}\mathbf{C} \rightarrow \mathbf{Q1'*} = (t_{[100]}, t_{[001]}, t_{[\frac{1}{2}\frac{1}{2}0]})\{1, \mathbf{C}, 1^{\frac{1}{*}}, \mathbf{C'*}\}$

Category (9): H + (Q-H) 1* + H1' + (Q-H) 1'*

 $\mathbf{Q} = \mathbf{C}\mathbf{C}, \ \mathbf{H} = (\mathbf{1}_{[100]}, \mathbf{1}_{[001]}, \mathbf{1}_{[1/2/20]}) \{1\} \rightarrow \mathbf{Q}\{\mathbf{H}\}\mathbf{1}^* = (\mathbf{1}_{[100]}, \mathbf{1}_{[001]}, \mathbf{1}_{[1/2/20]}) \{1, \mathbf{C}^*, \mathbf{1}', \mathbf{C}'^*\}$

 $\mathbf{Q} = \mathbf{C}\mathbf{C}, \ \mathbf{H} = (\mathsf{t}_{[100]}, \mathsf{t}_{[010]}, \mathsf{t}_{[001]})\{1, \mathbf{C}\} \rightarrow \mathbf{Q}\{\mathbf{H}\}\mathbf{1}^* = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[1/2/20]}^*)\{1, \mathbf{C}, \mathbf{1}', \mathbf{C}'\}$

 $\mathbf{Q} = CC, \mathbf{H} = (t_{[100]}, t_{[010]}, t_{[001]}) \{1, t_{[\frac{1}{2}\frac{1}{2}0]} \cdot C\} \rightarrow \mathbf{Q} \{\mathbf{H}\} \mathbf{1}^* =$

 $(t_{100}, t_{001}, t_{1/2})^{*} \{1, C^{*}, 1', C^{*}\}$

Category (10): H + (Q-H)1' + H1'* + (Q-H)1*

 $\mathbf{Q} = \mathbf{Cc}, \ \mathbf{H} = (t_{[100]}, t_{[001]}, t_{[1/21/20]})\{1\} \rightarrow \mathbf{Q}(\mathbf{H})\mathbf{1}^* = (t_{[100]}, t_{[001]}, t_{[1/21/20]})\{1, \mathbf{C}', 1^{*}, \mathbf{C}^*\}$

 $\mathbf{Q} = \mathbf{C}\mathbf{C}, \ \mathbf{H} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[001]}) \{1, \mathbf{C}\} \rightarrow \mathbf{Q}(\mathbf{H})\mathbf{1'*} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[1/2/20]}') \{1, \mathbf{C}, 1'^*, \mathbf{C}'^*\}$

 $\mathbf{Q} = CC, \, \mathbf{H} = (\dagger_{[100]}, \dagger_{[010]}, \dagger_{[001]}) \{1, \dagger_{[\frac{1}{2}/20]} \cdot C\} \rightarrow \mathbf{Q}(\mathbf{H})\mathbf{1'*} =$

 $(t_{[100]}, t_{[001]}, t_{[\frac{1}{2}}) \{1, C', 1'^*, C^*\}$

Category (11): H + (Q-H)1'*

 $\mathbf{Q} = CC, \ \mathbf{H} = (t_{[100]}, t_{[001]}, t_{[1/2/20]})\{1\} \rightarrow \mathbf{Q}\{\mathbf{H}\} = (t_{[100]}, t_{[001]}, t_{[1/2/20]})\{1, C^{**}\}$

 $\mathbf{Q} = \mathbf{CC}, \ \mathbf{H} = (\dagger_{[100]}, \dagger_{[001]}, \dagger_{[001]}) \{1, \mathbf{C}\} \rightarrow \mathbf{Q}\{\mathbf{H}\} = (\dagger_{[100]}, \dagger_{[001]}, \dagger_{[1/2]/20}]^*) \{1, \mathbf{C}\}$

 $\mathbf{Q} = \mathbf{CC}, \ \mathbf{H} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[001]}) \{1, \mathsf{t}_{[\frac{1}{2}\frac{1}{2}0]} \cdot \mathbf{C}\} \rightarrow \mathbf{Q}\{\mathbf{H}\} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[\frac{1}{2}\frac{1}{2}0]} \cdot *) \{1, \mathbf{C}^{**}\}$

Category (12): $H \cap K + (H-K)$ ^{*} + (K-H)¹ + (Q-(H+K))¹

 $\mathbf{Q} = \mathbf{CC}, \ \mathbf{H} = (\mathbf{1}_{[100]}, \mathbf{1}_{[010]}, \mathbf{1}_{[001]}) \{\mathbf{1}, \mathbf{C}\}, \ \mathbf{K} = (\mathbf{1}_{[100]}, \mathbf{1}_{[010]}, \mathbf{1}_{[001]}) \{\mathbf{1}, \mathbf{1}_{[\frac{1}{2}\frac{1}{2}0]}, \mathbf{C}\} \rightarrow \mathbf{Q}(\mathbf{H}) \{\mathbf{K}\} = \mathbf{CC}, \ \mathbf{H} = (\mathbf{1}_{[100]}, \mathbf{1}_{[010]}, \mathbf{1}_{[010]}, \mathbf{1}_{[010]}, \mathbf{1}_{[010]}, \mathbf{C}\}$

 $(t_{100}, t_{001}, t_{1/2})^{*} \{1, C^{*}\}$

 $\mathbf{Q} = \mathbf{CC}, \ \mathbf{H} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[1240]})\{1\}, \ \mathbf{K} = (\mathsf{t}_{[100]}, \mathsf{t}_{[010]}, \mathsf{t}_{[001]})\{1, \mathsf{t}_{[1240]}, \mathbf{C}\} \rightarrow \mathbf{Q}(\mathbf{H})\{\mathbf{K}\} = \mathbf{CC}, \ \mathbf{H} = (\mathsf{t}_{[100]}, \mathsf{t}_{[001]}, \mathsf{t}_{[100]}, \mathsf{t}_{[100]$

 $(t_{100}, t_{001}, t_{1/2})^{*} \{1, C'^{*}\}$

$$\mathbf{Q} = CC, \ \mathbf{H} = (t_{[100]}, t_{[001]}, t_{[1/2/20]})\{1\}, \ \mathbf{K} = (t_{[100]}, t_{[010]}, t_{[001]})\{1, C\} \rightarrow \mathbf{Q}(\mathbf{H})\{\mathbf{K}\} =$$

 $(t_{[100]}, t_{[001]}, t_{[\frac{1}{2}\frac{1}{2}0]}*){1, C'}$

 $\mathbf{Q} = CC, \ \mathbf{H} = (t_{[100]}, t_{[010]}, t_{[001]}) \{1, t_{[1/21/20]} \cdot C\}, \ \mathbf{K} = (t_{[100]}, t_{[010]}, t_{[001]}) \{1, C\} \rightarrow \mathbf{Q}(\mathbf{H}) \{\mathbf{K}\} = (t_{[100]}, t_{[010]}, t$

(†[100],†[001],†[½½0]'*){1,C'}

 $\mathbf{Q} = C_{C}, \mathbf{H} = (t_{[100]}, t_{[010]}, t_{[001]}) \{1, t_{[\frac{1}{2}\frac{1}{2}0]} \cdot C\}, \mathbf{K} = (t_{[100]}, t_{[001]}, t_{[\frac{1}{2}\frac{1}{2}0]}) \{1\} \rightarrow \mathbf{Q}(\mathbf{H}) \{\mathbf{K}\} = (t_{[100]}, t_{[010]}, t_{[\frac{1}{2}\frac{1}{2}\frac{1}{2}0]}) \{1\} \rightarrow \mathbf{Q}(\mathbf{H}) \{\mathbf{K}\} = (t_{[100]}, t_{[\frac{1}{2}\frac{1}{$

 $(t_{[100]}, t_{[001]}, t_{[1/2]/20]}){1, C'^*}$

 $\mathbf{Q} = CC, \mathbf{H} = (t_{100]}, t_{001]}, t_{1001}, t_{10$

 $(t_{[100]}, t_{[001]}, t_{[\frac{1}{2}})){1, C^*}$

Note that although 29 double antisymmetry space groups are generated from using Cc as a colorblind parent group, they are not all of unique types. This is because there exist proper affine transformations which map some of these into each other. We show this by applying the results of Section 3.10. To do this, we need to know the transformation matrices mapping the standard representative groups to the actual subgroups, and the affine normalizer groups of Cc and its index-2 subgroups. For Cc's three index-2 subgroups:

 $(t_{[100]}, t_{[001]}, t_{[1/2]/20]})$ {1} is type P1 and can be mapped from the standard P1 by

```
\begin{pmatrix} 1/2 & 1/2 & 0 & 0 \\ -1/2 & 1/2 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}
```

(t_[100],t_[010],t_[011]){1,c} is type Pc and can be mapped from the standard Pc by

```
\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}
```

 $(t_{100]}, t_{010]}, t_{001]}$ (1, $t_{1/2/20]}$ c} is type Pc and can be mapped from the standard Pc by

 $\begin{pmatrix} 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 1/4 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$

The subgroup of proper motions of the affine normalizer of Cc are:

$$\mathbf{N}_{\mathcal{A}^+} \left(\mathsf{Cc} \right) = \left\{ \begin{pmatrix} 2n_1 + 1 & 0 & 2n_2 + p & r \\ 0 & \pm 1 & 0 & (2n_3 + p)/4 \\ 2n_4 & 0 & 2n_5 + 1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} \in \mathcal{A}^+ : \ r, t \in \mathbb{R} \land n_i \in \mathbb{Z} \land (p = 0 \lor p = 1) \right\}$$

The subgroups of proper motions of the affine normalizers of the standard

representative groups of the two types of subgroups (P1 and Pc) are:

P1 normalizers:
$$\mathbf{N}_{\mathcal{A}^{+}} (P1) = \begin{cases} \binom{n_{11} & n_{12} & n_{13} & r}{n_{21} & n_{22} & n_{23} & s} \\ n_{31} & n_{32} & n_{33} & t \\ 0 & 0 & 0 & 1 \end{cases} \in \mathcal{A}^{+} : r, s, t \in \mathbb{R} \land n_{ij} \in \mathbb{Z} \end{cases}$$
Pc normalizers:
$$\mathbf{N}_{\mathcal{A}^{+}} (Pc) = \begin{cases} \binom{2n_{6} + 1 & 0 & 2n_{7} & r}{0 & \pm 1 & 0 & n_{8}/2} \\ n_{9} & 0 & 2n_{10} + 1 & t \\ 0 & 0 & 0 & 1 \end{cases} \in \mathcal{A}^{+} : r, t \in \mathbb{R} \land n_{i} \in \mathbb{Z} \end{cases}$$

Having collected all this information, we can now evaluate the proper affine equivalence of the 29 double antisymmetry groups generated from $\mathbf{Q} = \mathbf{Cc}$.

We know that groups from different categories can never be equivalent; therefore categories (1), (2), (4), (5) and (8) must contain only one type as only one group has been generated.

For category (3), we have three generated groups. Thus there are three pairs for which we can test for equivalence, $3\sim4$, $3\sim5$, and $4\sim5$. For group 3, **H** is P1 type whereas for 4 and 5 **H** is Pc type. Therefore, $3\sim4$ and $3\sim5$ are false. For $4\sim5$, we can evaluate:

$$\mathbf{Q}(\mathbf{H}_2) \sim \mathbf{Q}(\mathbf{H}_1) \equiv \mathbf{N}_{\mathcal{A}^+}(\mathbf{Q}) \cap T_{H_2} \mathbf{N}_{\mathcal{A}^+}(\mathbf{H}_0) T_{H_1}^{-1} \neq \emptyset$$

In this case,

$$T_{H_2}\mathbf{N}_{\mathcal{A}^+}(\mathbf{H}_{\mathbf{0}})T_{H_1}^{-1} = \left\{ \begin{pmatrix} 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 2n_6 + 1 & 0 & 2n_7 & r \\ 0 & \pm 1 & 0 & n_8/2 \\ n_9 & 0 & 2n_{10} + 1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}^{-1} \in \mathcal{A}^+: r, t \in \mathbb{R} \land n_i \in \mathbb{Z} \right\}$$

and

$$\mathbf{N}_{\mathcal{A}^+}\left(\mathbf{Q}\right) = \left\{ \begin{pmatrix} 2n_1 + 1 & 0 & 2n_2 + p & r \\ 0 & \pm 1 & 0 & (2n_3 + p)/4 \\ 2n_4 & 0 & 2n_5 + 1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} \in \mathcal{A}^+ : r, t \in \mathbb{R} \land n_i \in \mathbb{Z} \land (p = 0 \lor p = 1) \right\}$$

From substituting these in and simplifying, we can show that 4~5 is logically equivalent to the existence of a solution with a positive determinant to the following:

$$\begin{pmatrix} 2n_1+1 & 0 & 2n_2+p & r \\ 0 & \pm 1 & 0 & (2n_3+p)/4 \\ 2n_4 & 0 & 2n_5+1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 2n_6+1-n_9 & 0 & -1-2n_{10}+2n_7 & r-t \\ 0 & \pm 1 & 0 & (2n_8+1)/4 \\ n_9 & 0 & 2n_{10}+1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

There are clearly many solutions, e.g. one solution is where $n_2 = -1$, $n_{i\neq 2} = r = t = 0$, and p = 1. Thus, 4 and 5 are equivalent and therefore for category (3), there are only two types of groups where $\mathbf{Q} = Cc$. It is trivial to extend these results to show that categories (6), (7), (9), 10), and (11) similarly have two types. For category (12), we have six generated groups. Thus there are fifteen pairs for which we can test for equivalence. Only three of the fifteen have the same **H** and **K** types (26~25, 24~27, and 28~29) and therefore only these need to be evaluated using:

$$\mathbf{Q}(\mathbf{H}_{1})\{\mathbf{K}_{1}\} \sim \mathbf{Q}(\mathbf{H}_{2})\{\mathbf{K}_{2}\} \equiv \mathbf{N}_{\mathcal{A}^{+}}(\mathbf{Q}) \cap T_{H_{2}}\mathbf{N}_{\mathcal{A}^{+}}(\mathbf{H}_{0})T_{H_{1}}^{-1} \cap T_{K_{2}}\mathbf{N}_{\mathcal{A}^{+}}(\mathbf{K}_{0})T_{K_{1}}^{-1} \neq \emptyset$$

For 26~25,

$$\begin{split} T_{H_2}\mathbf{N}_{\mathcal{A}^+}(\mathbf{H}_{\mathbf{0}})T_{H_1}^{-1} &= \left\{ \begin{pmatrix} 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & \frac{1}{4} \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 2n_6 + 1 & 0 & 2n_7 & r \\ 0 & \pm 1 & 0 & n_8/2 \\ n_9 & 0 & 2n_{10} + 1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}^{-1} \in \mathcal{A}^+ : r, t \in \mathbb{R} \land n_i \in \mathbb{Z} \right\}, \\ T_{K_2}\mathbf{N}_{\mathcal{A}^+}(\mathbf{K}_{\mathbf{0}})T_{K_1}^{-1} &= \left\{ \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} n_{11} & n_{12} & n_{13} & r \\ n_{21} & n_{22} & n_{23} & s \\ n_{31} & n_{32} & n_{33} & t \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 & 0 \\ -\frac{1}{2} & \frac{1}{2} & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}^{-1} \in \mathcal{A}^+ : r, s, t \in \mathbb{R} \land n_{ij} \in \mathbb{Z} \right\}, \end{split}$$

and

$$\mathbf{N}_{\mathcal{A}^+}\left(\mathbf{Q}\right) = \begin{cases} \begin{pmatrix} 2n_1 + 1 & 0 & 2n_2 + p & r \\ 0 & \pm 1 & 0 & (2n_3 + p)/4 \\ 2n_4 & 0 & 2n_5 + 1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} \in \mathcal{A}^+ : r, t \in \mathbb{R} \land n_i \in \mathbb{Z} \land (p = 0 \lor p = 1) \end{cases}.$$

From substituting these in and simplifying, we can show that 26~25 is logically equivalent to the existence of a solution with a positive determinant to the following:

$$\begin{pmatrix} 2n_1+1 & 0 & 2n_2+p & r \\ 0 & \pm 1 & 0 & (2n_3+p)/4 \\ 2n_4 & 0 & 2n_5+1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 2n_6+1-n_9 & 0 & -1-2n_{10}+2n_7 & r-t \\ 0 & \pm 1 & 0 & (2n_8+1)/4 \\ n_9 & 0 & 2n_{10}+1 & t \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} n_{11}-n_{31} & n_{12}-n_{32} & n_{13}-n_{33} & r-t \\ n_{21} & n_{22} & n_{23} & s+1/4 \\ n_{31} & n_{32} & n_{33} & t \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

There are clearly many solutions, e.g. one solution is where $n_2 = -1$, $n_{i\neq 2} = r = t = s = 0$, p = 1, $n_{i=j} = 1$, and $n_{i\neq j} = 0$. Thus 25 and 26 are equivalent. Since 24, 27, 28 and 29 can be related to 25 and 26 by automorphisms of **1'1***, 26~25 implies 24~27

and 28~29. Therefore there are only three types of category (12) groups and a total of twenty double antisymmetry space group types for $\mathbf{Q} = Cc$.

3.14 Equivalence classes, proper affine classes (types), Mackay groups, and color-permuting classes

An equivalence relation can be used to partition a set of groups into equivalence classes. For example, an equivalence relation can be applied to partition the set of crystallographic space groups (which is uncountably infinite) into a finite number of classes. The proper affine equivalence relation is used to classify space groups into 230 proper affine classes or "types". Proper affine equivalence relation be defined as: two groups, **G**₁ and **G**₂, are equivalent if and only if **G**₁ can be bijectively mapped to **G**₂ by a proper affine transformation, *a*.

$$\mathbf{G}_2 \sim \mathbf{G}_1 \equiv \exists a \in \mathcal{A}^+ : (\mathbf{G}_2 = a\mathbf{G}_1 a^{-1})$$

If it is known that G_1 and G_2 have the same colorblind parent group Q, then, instead of using the entire proper affine group \mathcal{A}^+ , it is sufficient to use the subgroup of proper motions of the affine normalizer group of Q, denoted $N_{\mathcal{A}^+}(Q)$.

The proper affine equivalence relation does not allow for any permutations of anti-identities. Other works give another set of equivalence classes of antisymmetry groups called Mackay groups ^{120,121,123}. The equivalence relation of Mackay groups allows some color permutations in addition to proper affine transformation. For double antisymmetry, the Mackay equivalence relation allows for 1' and 1* to be permutated, *i.e.* all the primed operations become starred and vice versa:

$$\mathbf{G}_2 \sim \mathbf{G}_1 \equiv \exists a \in \mathcal{A}^+ \land \exists p \in \{1, \mathbf{1}' \leftrightarrow \mathbf{1}^*\} : (\mathbf{G}_2 = ap(\mathbf{G}_1)a^{-1})$$

The Mackay equivalence relation does not allow for 1^{+*} to be permutated ¹²³. Note that Radovic & Jablan do give the Mackay equivalence relation as permuting "anti-identities" but 1^{+*} is not considered an anti-identity in their work (it is simply the product of 1' and 1^{*}). They also conclude that Mackay groups are the minimal representation of "Zamorzaev groups". This seems potentially inconsistent with the aforementioned restriction on color permutation. If we instead allow for all possible color permutations that preserve the group structure of **1'1***, *i.e.* the automorphisms of **1'1***, then we can clearly further reduce the representation beyond that of the Mackay groups, contrary to what has been claimed. This is demonstrated by Zamorzaev & Palistrant's listing of double antisymmetry space group generating sets¹¹⁰. In their listing, they gave only those sets which were unique up to the automorphisms of **1'1***. Such a listing only needs to contain 1846 **Q(H){K}** generating sets, far fewer than the 5005 Mackay equivalence classes of **Q(H){K** groups.

If all possible color permutations that preserve the group structure of 1'1*, *i.e.* the automorphisms of 1'1*, are allowed, then the equivalence relation can be expressed as:

 $\mathbf{G}_2 \sim \mathbf{G}_1 \equiv \exists a \in \mathcal{A}^+ \land \exists p \in \operatorname{Aut}(\mathbf{1}'\mathbf{1}^*) : (\mathbf{G}_2 = ap(\mathbf{G}_1)a^{-1})$

This proper affine *color equivalence relation* results in 1846 classes for category (12) **Q(H){K}** groups. The equivalence classes of this kind of relation are similar to what Koptsik & Shubnikov refer to as "Belov groups"¹²⁴.

Generalized to an arbitrary coloring scheme, \mathbf{P} , the color equivalence relation be defined as:

$$\mathbf{G}_2 \sim \mathbf{G}_1 \equiv \exists a \in \mathcal{A}^+ \land \exists p \in \operatorname{Aut}(\mathbf{P}) : (\mathbf{G}_2 = ap(\mathbf{G}_1)a^{-1})$$

The advantage of using the color equivalence relation to reduce the number of equivalence classes becomes greater as the number of colors (the order of **P**) increases. For example, for non-trivial double antisymmetry space groups (where $\mathbf{P} \cong \mathbb{Z}_2^2$ and thus $|\mathbf{P}| = 4$), there are 9507 proper affine equivalence classes, 5005 Mackay equivalence classes, and 1846 color equivalence classes. Whereas for non-trivial sextuple antisymmetry space groups (where $\mathbf{P} \cong \mathbb{Z}_2^6$ and thus $|\mathbf{P}| = 64$), there are 419,973,120 proper affine equivalence classes, 598,752 Mackay equivalence classes, and just 1 color equivalence class. Although the number of colors only increased from 4 to 64 by going from non-trivial double antisymmetry space groups to non-trivial sextuple antisymmetry space groups, the number of proper affine classes increased from 9507 to 419,973,120 whereas the number of color equivalence classes actually decreased from 1846 to 1.

Although these color-permuting equivalence relations reduce the number of equivalence classes significantly, they are not suitable when the differences between the colors are important. With time-reversal as 1' and distortion-reversal as 1*, the differences are clearly very important. However, there may be

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applications where the color equivalence relation is suitable, for example, in making patterns for aesthetic purposes.

3.15 Color Automorphisms of Double Antisymmetry

The automorphism group of **1'1*** and the subgroups thereof are discussed in this section. **1'1*** is isomorphic to $\mathbb{Z}_2 \times \mathbb{Z}_2$. We can use this isomorphism to derive Aut(**1'1***). Let *m* be the isomorphism of **1'1*** onto $\mathbb{Z}_2 \times \mathbb{Z}_2$ which maps 1 to (0,0), 1' to (1,0), 1* to (0,1), and 1'* to (1,1). Using this isomorphism, the automorphism group of **1'1*** can be solved for from the automorphism group of $\mathbb{Z}_2 \times \mathbb{Z}_2$:

$$\operatorname{Aut}(\mathbf{1}'\mathbf{1}^*) = \{m^{-1}bm : b \in \operatorname{Aut}(\mathbb{Z}_2 \times \mathbb{Z}_2)\}\$$

The automorphism group of $\mathbb{Z}_2 \times \mathbb{Z}_2$ is $\mathbf{GL}(2,\mathbb{Z}_2)$, the general linear group of degree 2 over the field of 2 elements (or more precisely is isomorphic to it). $\mathbf{GL}(2,\mathbb{Z}_2)$ is represented by these six matrices: $\left\{\begin{pmatrix}1 & 0\\0 & 1\end{pmatrix}, \begin{pmatrix}1 & 1\\1 & 0\end{pmatrix}, \begin{pmatrix}0 & 1\\1 & 1\end{pmatrix}, \begin{pmatrix}0 & 1\\1 & 1\end{pmatrix}, \begin{pmatrix}1 & 0\\1 & 1\end{pmatrix}\right\}$. Using *m*, we can solve for the **1'1*** automorphism implied by each of these matrices. As an example, consider the **1'1*** automorphism, $m^{-1}\begin{pmatrix}1 & 1\\1 & 0\end{pmatrix}m$, implied by the $\mathbb{Z}_2 \times \mathbb{Z}_2$ automorphism $\begin{pmatrix}1 & 1\\1 & 0\end{pmatrix}$: $\begin{pmatrix}1 & 1\\1 & 0\end{pmatrix}m$, implied by the $\mathbb{Z}_2 \times \mathbb{Z}_2$ automorphism $\begin{pmatrix}1 & 1\\1 & 0\end{pmatrix}$:

$$(0,0) \xrightarrow{(1-0)} (0,0) \leftrightarrow 1 \xrightarrow{(1-0)} 1$$
$$(1,0) \xrightarrow{\begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}} (1,1) \leftrightarrow 1' \xrightarrow{m^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}} 1'^{*}$$
$$(0,1) \xrightarrow{\begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}} (1,0) \leftrightarrow 1^{*} \xrightarrow{m^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}} 1'$$

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$$(1,1) \xrightarrow{\begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}} (0,1) \leftrightarrow 1'^* \xrightarrow{m^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}} m \xrightarrow{1^*}$$

Thus, $m^{-1} \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix} m$ is the permutation $\begin{pmatrix} 1' & 1^* & 1'^* \\ 1'^* & 1' & 1^* \end{pmatrix}$. Or using one-line notation, (1'*, 1', 1*). Applying this to each element of **GL**(2, \mathbb{Z}_2), we find that $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$, $\begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}$, $\begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}$, $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}$, $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\begin{pmatrix} 1 & 1 \\ 1 &$

The subgroups of $GL(2, \mathbb{Z}_2)$ can be used to find the subgroups of $Aut(1'1^*)$. The subgroups of $GL(2, \mathbb{Z}_2)$:

Index=6 (order = 1): $\{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\}$ Index=3 (order=2): $\{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\}, \{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}\}, and <math>\{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 \\ 1 & 1 \end{pmatrix}\}$ Index=2 (order=3): $\{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}\}$ Index=1 (order=6): $\{\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}, \begin{pmatrix} 1 & 1 \\ 1 & 0 \end{pmatrix}\}$

imply the following Aut(1'1*) subgroups:

Index=6 (order = 1): {(1', 1*, 1'*)}

Index=3 (order=2): $\{(1', 1^*, 1'^*), (1', 1^*, 1^*)\}, \{(1', 1^*, 1'^*), (1^*, 1', 1'^*)\}, and <math>\{(1', 1^*, 1'^*), (1'^*, 1^*, 1')\}$

Index=2 (order=3): {(1', 1*, 1'*), (1*, 1'*, 1'), (1'*, 1', 1*)}

Index=1 (order=6): {(1', 1*, 1'*), (1', 1'*, 1*), (1*, 1', 1'*), (1*, 1'*, 1'), (1*, 1'*, 1'), (1'*, 1',

1*), (1'*, **1***, **1**')}

For each line of generators, Zamorzaev & Palistrant¹¹⁰ give the number of types represented by that line, which corresponds to the order of a subgroup of Aut(**1'1***). Zamorzaev & Palistrant do not give which automorphisms need to be

applied to generate these types. However, any valid partition of $Aut(1'1^*)$ by generated type must have an associated subgroup by which the elements of the members of the partition must be related, i.e. said partition is a coset decomposition of $Aut(1'1^*)$.

Applying this understanding, we find that for lines of generators which result in 1, 2, or 6 types, there is only one valid partition of Aut(1'1*) by generated type because there is only one coset decomposition for index 1, 2, and 6 respectively. For lines of generators which result in 3 types, there are three possible coset decompositions (technically three left and three right, but we can only choose to use left or right multiplication on the generating set, not both).

The results from this analysis for a line of generators can be summarized as follows:

(1', 1*, 1'*) (1*, 1'*, 1') (1'*, 1', 1*) (1', 1'*, 1*) (1*, 1', 1'*) (1'*, 1*, 1')

- 1 type = all permutations yield groups of the same type
- 2 types = permutations in the same row yield groups of the same type
- 3 types = permutations in the same row yield distinct types of groups
- 6 types = all permutations are distinct types of groups

This method can be generalized to multiple antisymmetry and other color symmetries. For double antisymmetry, it would have been simpler to check which permutations of anti-identities preserved the group structure of 1'1*. As it turns out, they all do, *i.e.* Aut(1'1*) \cong S₃. This will not work *l*-tuple antisymmetry for l > 2. For *l*-tuple antisymmetry for l > 2: the automorphism group of \mathbb{Z}_2^n is isomorphic to general linear group of degree *n* over the field of 2 elements, **GL**(*n*, \mathbb{Z}_2), and a similar method can thus be employed.

3.16 Using the machine-readable file

All 38,290 double antisymmetry space groups generated by applying formulae in Table 1 to the standard representative group of each of the 230 crystallographic space group types are listed in "DASGMachineReadable.txt". Each group is represented as eight lines; the entire file contains a total of 306,320 lines (8*38,290).

The first line of each set of eight contains three numbers: the serial number of the type (1 to 17,803), the "setting" number to identify groups with the same type (1 to the number of groups in that type), and the number of the category of the group (1 to 12).

The second line contains five numbers: the space group number of **Q** (1 to 230), the space group number of **H** (1 to 230), the space group number of **K** (1 to 230), the space group number of **L** (1 to 230), and the space group number of **R** (1 to 230). **Q**, **H**, and **K**, have the same meaning as previously given in Table 1. **R** is **H**∩**K** and is therefore an index-4 subgroup of **Q**. **L** is an index-2 subgroup of **Q** which is equivalent to **Q**-(**H**+**K**)+**R**. If a number is not applicable to the current category then "0" is given.

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The third line contains 80 numbers. These are to be partitioned into five 4by-4 matrices representing the transformations from \mathbf{Q}_0 , \mathbf{H}_0 , \mathbf{K}_0 , \mathbf{L}_0 , and \mathbf{R}_0 , onto \mathbf{Q} , H, K, L, and R respectively, e.g. the third matrix is T_H such that $\mathbf{H} = T_H \mathbf{H}_0 T_{H^{-1}}$. \mathbf{Q}_0 , \mathbf{H}_0 , K₀, \mathbf{L}_0 , and \mathbf{R}_0 are standard representative groups as given in first 230 groups of this listing, i.e. the category 1) groups (also these standard representative groups of the conventional space group types in the International Tables for Crystallography). Since $\mathbf{Q}_0 = \mathbf{Q}$ for all groups in this listing, the first matrix is always an identity matrix. If a matrix is not applicable to the current category then zeros are given for all elements of the matrix.

The fourth line contains between three and six numbers. These give the color of the translation subgroup generators; 1 means colorless (coupled with 1), 2 means primed (colored with 1'), 3 means starred (colored with 1*), and 4 means prime-starred (colored with 1'*). The translation indicated by each position is depends on the lattice type of **Q** as follows:

	1 st position	2 nd position	3 rd position	4 th position	5 th position	6 th position
Р	t _[100]	† _[010]	† _[001]			
С	t _[100]	† _[010]	† _[001]	† _{[½1/2} 0]		
А	t _[100]	† _[010]	t _[001]	† _[0½½]		
1	t _[100]	† _[010]	† _[001]	† _{[½½½]/2}]		
F	t _[100]	† _[010]	† _[001]	† _[01/21/2]	† _[½0½]	† _{[½½]/2} 0]
R	t _[100]	† _[010]	† _[001]	$\dagger_{[\frac{2}{3}\frac{1}{3}\frac{1}{3}]}$	$\dagger_{[\frac{1}{3}^{2}/3^{2}/3]}$	

The 4th through 6th positions of the fourth line are always centering translations (those with non-integer values). It is only necessary to use the first three positions generally because the coloring of the centering translations is also given in the fifth through eighth lines. The fifth line contains a list of numbers whose length is a multiple of 16. This list is to be partitioned into 4-by-4 matrices representing the matrix form of the colorless operations. The sixth, seventh, and eighth lines are to be similarly partitioned and represent the matrix form of primed, starred and prime-starred operations respectively.

3.17 Full symmetry diagram and property listing

The section discusses the tables of symmetry diagrams and properties of the antisymmetry available double space groups online at http://sites.psu.edu/gopalan/research/symmetry/ "Double by clicking Antisymmetry Space Group Diagrams and Wyckoff orbits (280MB)"). The structure of the tables is similar to the tables found in the International Tables for Crystallography Volumes A¹⁰¹ and E¹⁰⁶, and in tables of magnetic space groups¹⁰².



Figure 3-9. Part 1 of table of crystallographic properties of the double antisymmetry space group $P(1,1^*,1)mm'a^*$, No. 10977.

Po	sitio	ns	Coordinates	
8	1	1	$\{x, y, z\}[a, b, c][d, e, f]$	$\{\bar{x}+\frac{1}{2}, \bar{y}, z\}[\bar{a}, \bar{b}, c][\bar{d}, \bar{e}, f]$
			$\{ar{x},y,ar{z}\}[ar{a},b,ar{c}][ar{d},e,ar{f}]$	$\{x+\frac{\overline{1}}{2},\overline{y},\overline{z}\}[a,\overline{b},\overline{c}][d,\overline{e},\overline{f}]$
			$\{\bar{x}, \bar{y}, \bar{z}\}[a, b, c][d, e, f]$	$\{x+\frac{1}{2},y,\bar{z}\}[\bar{a},\bar{b},c][\bar{d},\bar{e},f]$
			$\{x, \bar{y}, z\}[\bar{a}, b, \bar{c}][\bar{d}, e, \bar{f}]$	$\{\bar{x}+\frac{\bar{1}}{2},y,z\}[a,\bar{b},\bar{c}][d,\bar{e},\bar{f}]$
4	k	<i>m</i>	$\{\frac{1}{4}, y, z\}[a, 0, 0][d, 0, 0]$	$\{\frac{1}{4}, \bar{y}, \bar{z}\}[\bar{a}, 0, 0][\bar{d}, 0, 0]$
			$\{\frac{3}{4}, y, \bar{z}\}[\bar{a}, 0, 0][\bar{d}, 0, 0]$	$\{\frac{3}{4}, \bar{y}, \bar{z}\}[a, 0, 0][d, 0, 0]$
4	j	$. m'^{*} .$	$\{x, \frac{1}{2}, z\}[a, 0, c][d, 0, f]$	$\{\bar{x}+\frac{1}{2},\frac{1}{2},z\}[\bar{a},0,c][\bar{d},0,f]$
			$\{ar{x}, rac{1}{2}, ar{z}\}[ar{a}, 0, ar{c}][ar{d}, 0, ar{f}]$	$\{x+\frac{1}{2},\frac{1}{2},\bar{z}\}[a,0,\bar{c}][d,0,\bar{f}]$
4	i	. <i>m</i> ′.	${x,0,z}[a,0,c][0,e,0]$	$\{\bar{x}+\frac{1}{2},0,z\}[\bar{a},0,c][0,\bar{e},0]$
			$\{\bar{x}, 0, \bar{z}\}[\bar{a}, 0, \bar{c}][0, e, 0]$	${x+\frac{1}{2},0,\bar{z}}[a,0,\bar{c}][0,\bar{e},0]$
4	h	. 2* .	$\{0, y, \frac{1}{2}\}[0, b, 0][d, 0, f]$	$\{rac{1}{2},ar{y},rac{1}{2}\}[0,ar{b},0][ar{d},0,f]$
			$\{0, ar{y}, rac{1}{2}\}[0, b, 0][d, 0, f]$	$\{\frac{1}{2}, y, \frac{1}{2}\}[0, \bar{b}, 0][\bar{d}, 0, f]$
4	g	. 2* .	$\{0, y, 0\}[0, b, 0][d, 0, f]$	$\{rac{1}{2},ar{y},0\}[0,ar{b},0][ar{d},0,f]$
			$\{0, ar{y}, 0\}[0, b, 0][d, 0, f]$	$\{\frac{1}{2}, y, 0\}[0, \bar{b}, 0][\bar{d}, 0, f]$
2	f	$m m'^* 2'^*$	$\{\frac{1}{4}, \frac{1}{2}, z\}[a, 0, 0][d, 0, 0]$	$\{rac{3}{4},rac{1}{2},ar{z}\}[ar{a},0,0][ar{d},0,0]$
2	e	<i>m m</i> ′ 2′	$\{\frac{1}{4}, 0, z\}[a, 0, 0][0, 0, 0]$	$\{rac{3}{4},0,ar{z}\}[ar{a},0,0][0,0,0]$
2	d	$.2^{*}/m^{\prime *}$.	$\{0, rac{1}{2}, rac{1}{2}\}[0, 0, 0][d, 0, f]$	$\{rac{1}{2},rac{1}{2},rac{1}{2}\}[0,0,0][ar{d},0,f]$
2	с	$.2^{*}/m'$.	$\{0,0,rac{1}{2}\}[0,0,0][0,0,0]$	$\{rac{1}{2},0,rac{1}{2}\}[0,0,0][0,0,0]$
2	b	$.2^{*}/m^{\prime *}$.	$\{0,rac{1}{2},0\}[0,0,0][d,0,f]$	$\{rac{1}{2},rac{1}{2},0\}[0,0,0][ar{d},0,f]$
2	a	$.2^{*}/m'$.	$\{0,0,0\}[0,0,0][0,0,0]$	$\{rac{1}{2},0,0\}[0,0,0][0,0,0]$

Figure 3-10. Part 2 of table of crystallographic properties of the double antisymmetry space group $P(1,1^*,1)mm'a^*$, No. 10977.

The tables contain crystallographic properties for all 17,803 double antisymmetry

space group types. Each table contains:

- (1) Headline
- (2) Lattice diagram
- (3) Diagram of symmetry elements and general position diagram
- (4) Symmetry operations
- (5) General and special positions.

3.17.1 Headline

A headline is placed on the left top of the first page for each table. Each headline consists of two lines, which read from left to right. A headline consists of the following information:

First line:

- The serial number of the double antisymmetry space group.
 The serial numbers of the double antisymmetry space groups follow the numbering system of VanLeeuwen et al.³⁷.
- (2) International (Hermann-Mauguin) symbol of the double antisymmetry space group.

The International symbols are those introduced by VanLeeuwen et al. The notation specifies the representative group of the group type. The symmetry operations of the representative group are given later in the section of symmetry operations.

(3) X-ray diffraction symmetry group.

This is the symmetry which would be expected to be indicated by the typical methods of analysis of x-ray diffraction patterns (one of the 230 conventional space groups). This group comes from converting all primed operations to colorless operations (because x-ray scattering is invariant under the action of time-reversal) and removing all starred and primed-starred operations (because x-ray scattering is non-invariant under the action of rotation-reversal). If the standard setting of the X-ray diffraction symmetry group differs from that of the double antisymmetry space group, the affine transformation relating the two is given. The notation for this transformation is meant to be short-hand for the 4x4 augmented matrix of the transformation, *i.e.*

$$\begin{pmatrix} R_{11} & R_{12} & R_{13} & t_1 \\ R_{21} & R_{22} & R_{23} & t_2 \\ R_{31} & R_{32} & R_{33} & t_3 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

would be given as

$$R_{11}a + R_{12}b + R_{13}c + t_1, R_{21}a + R_{22}b + R_{23}c + t_2, R_{31}a + R_{32}b + R_{33}c + t_3.$$

Second line:

- (1) The serial number of the colorblind parent group type in the International Tables for Crystallography, Vol. A¹⁰¹ (abbreviated as ITC-A). The colorblind parent group of a double antisymmetry space group is the space group based on which the double antisymmetry space group is generated. It is denoted by Q by VanLeeuwen et al. The colorblind parent group of a double antisymmetry space group can be derived from the double antisymmetry space group by substituting all double identities coupled with the symmetry operations with identities.
- (2) double antisymmetry point group symbol to which the space group belongs
- (3) The name of the crystal system of the group

For example, the headline for No. 10977 from Figure 3-9 is shown below.

No. 10977	$P(1, 1^*, 1)mm'a^*$	$Pmmn_{a,2b+\frac{1}{2},c}$	
SG. 51	<i>mm</i> ′ <i>m</i> 1*	Orthorhombic	×

z

The serial number of the type is 10977, the modified International (Hermann-Mauguin) symbol is $P(1,1^*,1)mm'a^*$, the colorblind parent group is space group No. 51 in ITC-A, the double antisymmetry point group in which the group belongs is $mm'm1^*$, and the crystal system of the group is orthorhombic.

3.17.2 Lattice diagram

A three-dimensional lattice diagram is given for each double antisymmetry space group in the upper right corner of the first page, which describes the conventional lattice cell of the colorblind parent group of the group with the generators of the translation subgroup of the group. For example, the lattice diagram of group $P(1,1^*,1)mm'a^*$ is shown in Figure 3-11. The conventional lattice cell of the group type is orthorhombic and the generators of the translation subgroup are (1, 0, 0), $(0, 1, 0)^*$, and (0, 0, 1). The color of each arrow indicates whether it is a pure colorless translation (black), a primed translation (red), a starred translation (blue), or a prime-starred translation (green). For instance, the blue arrow along y in Figure 3-11 represents a starred translation along y.



Figure 3-11. Lattice diagram of double antisymmetry space group P(1,1*,1)mm'a*, No. 10977.

The diagram shows the orthorhombic $P(1,1^*,1)$ lattice. The unit translation along y-axis is colored blue, which shows the translation is coupled with the anti-identity 1^* .

3.17.3 Diagrams of symmetry elements and general positions

Following the headline and the lattice diagram, diagrams of symmetry elements and general positions are given. The symmetry element diagrams show the relative locations and orientations of the symmetry elements and the general position diagrams show locations of a set of general positions.

The arrangement of the diagrams for different crystal systems are shown in Section 3.17.8. The projection direction for all diagrams is perpendicular to the plane of the figure. The *b*-axis is selected as the unique axis for monoclinic groups. Symmetry element diagrams projected along *a*, *b*, and *c* directions are given for triclinic, monoclinic and orthorhombic groups. Symmetry element diagrams projected along the c-axis are given for tetragonal, hexagonal, and trigonal groups. General position diagrams projected along c-axis are given for all groups.

The color of a graphical symbol of a symmetry element indicates that the symmetry element is colored with an anti-identity associated with that color or not coupled with any anti-identity if the color is black. Similarly, the color of a graphical symbol of a general position indicates that the position is generated from the starting position by a symmetry operation coupled with anti-identity associated with that color or not coupled with any anti-identity if the color is black. The colors associated with antisymmetry identities follow the coloring schemes of VanLeeuwen et al. ³⁷.

Two types of unit cell are defined for a double antisymmetry space group. Here we define the conventional unit cell of the colorblind parent group of a double antisymmetry space group as the *colorblind unit cell*, and the unit cell that can fill the space with colorless translations as the *colorless unit cell*. A colorless translation is a translation that is not coupled with any anti-identity. A colored translation is a translation coupled with one of the three anti-identities, and is printed in the same color as the anti-identity to denote the coupling. The colorblind unit cell and the colorless unit cell are different for double antisymmetry space groups in which the colorblind unit cell translations are coupled with anti-identities. For example, in a P(1,1*,1) lattice, the colorblind unit cell is the same as its colorblind parent space group, which has a size of 1x1x1, while the colorless unit cell has a size of 1x2x1.

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The diagrams only consider the unit cell of the colorblind parent group of a double antisymmetry space group, i.e. the colorblind unit cell. The diagrams only show the symmetry elements within the colorblind unit cell, because the diagrams can be easily extended as the symmetry element diagrams are periodic in the directions of translation, and general position diagrams are periodic in the direction of a colorless translation and the color alternating according to color operation rule in the direction of a colored translation.

3.17.4 Diagrams of symmetry elements

The symbols used in diagrams of symmetry elements are extensions of those used in ITC-A. Detailed meanings of the symbols are discussed in Section 3.17.9.

The heights of centers of symmetry, rotoinversions, and axes and planes parallel to the plane of projection are printed next to the graphical symbol if the heights are non-zero. Some symmetry elements sit on top of each other in the projected diagram. The way heights are provided for these elements are listed in Table 3-12.

If a group has a colored unit cell translation and there is a mirror plane which contains the translation, combination of the translation and the mirror operation will result in a glide plane with a glide vector of colorblind unit cell translation. Such glide vectors are not shown in the diagrams as they can be derived from the original two operations. Because these two operations share

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the same plane showing both would unnecessarily complicate these diagrams. This also applies to any screw axes that come from a rotation axes coupled with a colored unit cell translation. The main benefit of this way of presenting the symmetry element diagrams is that the diagram of a double antisymmetry space group will show exactly the same elements as symmetry element diagram of its colorblind parent groups, with only additional colors to indicate the coupled anti-identities.

3.17.5 Diagrams of general positions

The symbols used in diagrams of general positions are extensions of those used in ITC-A. Each position is represented by a circle colored with the color of the position and a height notation beside the circle indicating the z-component of the position. For positions with z-component of "+z" or "-z", the height notation is "+" or "-" respectively. For positions with z-component of "h+z" or "h-z", the height notation is "h+" or "h-" respectively. If two general positions have the same x and y component and z components of +z and -z respectively, the two positions are represented as Φ . Each half of the symbol correspond to a unique position. The height notations are placed on two sides of the symbol respectively. For positions with respect to the starting position, a comma is added into the circle or the half of the circle that represents that position.



Figure 3-12. General position diagram for the double antisymmetry space group $P(1,1^*,1)mm'a^*$, No. 10977.

3.17.6 Symmetry operations

The modified ITC-A notation and Seitz notation for the symmetry operations are listed under the heading *Symmetry operation*. The symbolism follows Section 11.1.2 of ITC-A with the addition of the use of prime, star, and prime-star to denote coupled anti-identities. For glide planes and screw axes, the glide and screw vectors are given in unit of the length of the colorblind unit cell. In addition, a Seitz notation is also given for each symmetry operation. For double antisymmetry space groups with centered cells, the symmetry operations are given in several blocks. Groups without centering translations only have one block. For groups with centering translations, the number of blocks in addition to the origin (0, 0, 0)+ block equals to the number of the centering translations. For example, in a group with colorless body centering translations, two blocks (0, 0, 0)+ and (1/2, 1/2, 1/2)+ are shown. The transformations of symmetry operation are explicitly given in the notations, so readers do not need to add these centering translations to the notations.

3.17.7 General and special positions with spin vectors and roto vectors

Because this work pre-dates the development of distortion symmetry, Wyckoff positions are listed with "roto-vectors".

The position table of a double antisymmetry space group under *Positions* consists of general positions and special positions. These positions are called Wyckoff positions. The first block of the table is the general positions, which are the points that are left invariant only by identity operation or colored identity operations. The remaining blocks of the table are the special positions, which are the points that are left invariant by at least one non-identity operation. For each entry, the columns contains the following information from left to right.

a. Multiplicity of the Wyckoff position:

The multiplicity is the number of equivalent positions in the conventional unit cell of the colorblind parent space group of the double antisymmetry space group.

b. Wyckoff Letter:

The letter is a coding scheme for the blocks of positions, starting with a at the bottom block and continuing upwards in alphabetical order.

c. Oriented site-symmetry symbol:

The site symmetry group of the first position of each block of positions is given by an oriented symbol. The group is isomorphic to a subgroup of the point group of the double antisymmetry space group. The symbol shows how the symmetry elements of the site symmetry group are oriented at the site. The symmetry element symbol was placed according to the sequence of symmetry directions in the space group symbol. The symmetry directions that do not contribute any element to the site symmetry are represented by dots.

d. Coordinates and vectors on sites :

For each block of positions, the coordinates of the positions are given. Immediately to the right of each set of coordinates are two sets of components of two types of symmetry-allowed vectors at that position. The types of vectors are spin vector and roto vector placed on the left and right respectively. The properties of the two types of vectors are listed in e. Table 3-5. Then the components of the two types of vectors at the other positions are determined by applying the symmetry operations to the components of the corresponding vector at the first position.

Type of vector	Axial or polar	Inverted by 1'	Inverted by 1*
Spin vector	Axial	Yes	No
Roto vector	Axial	No	Yes

Table 3-5. Properties of two types of vectors listed in Wyckoff position table

For double antisymmetry space groups with centered cells, the centering translations such as (0,0,0)+ (1/2,1/2,1/2)'+ are listed above the ordinate triplets. The symbol "+" means that the components of these centering translation coordinates should be added to the listed coordinate triplets.

3.17.8 Schematic representations of diagram arrangement for different crystal systems

Schematic representations of the general-positions and symmetry-elements diagrams for different crystal systems (**G** = general position diagram)

Triclinic:



Monoclinic:





Orthorhombic:



Trigonal, Hexagonal and Rhombohedral:



3.17.9 Double antisymmetry space group diagram symbols

Most symbols used in the double antisymmetry space group diagrams have the same shapes as those used in ITC-A. The symbols are colored according to the anti-identity coupled with the operation. Extra symbols come from colored unit cell translations on the projection direction of the diagrams. When the unit cell translation is coupled with an anti-identity, there will be symmetry elements with different colors that are located at the same position on the projection plane but at different positions along the projection direction. Both the original and the extra symbols used are listed in the following tables (Table 3-6 to Table 3-12). The symbols are based on a symmetry elements font *cryst* created by Ulrich Müller from http://www.iucr.org/resources/symmetry-font.

For simplicity, any symmetry element that has only one color associated with it is represented by a symmetry element coupled with 1' (red), in Table 4-10. 1' can be substituted by identity or any anti-identity (1', 1*, or 1'*) and the coloring should be substituted (to black, red, blue, or green) respectively. Similarly, symmetry elements with two colors are represented by symmetry elements with 1' and 1* (red and blue) in Table 4-10 where 1' and 1* can be substituted by any two anti-identities and the colorings should be substituted respectively.

Symmetry axis	Graphical symbol	Screw vector of a right-handed screw axis in units of colorblind unit cell translation parallel to the axis	Printed symbol
2-fold primed rotation axis	←→	None	2'
2-fold primed screw axis		1/2	21'
4-fold primed rotation axis	╡┯╻╴╴╸╸	None	4'
4-fold primed screw axis		1/4	41'
4-fold primed screw axis		2/4	42'
4-fold primed screw axis		3/4	43'
4-bar primed inversion		None	4 '

Table 3-6. Symmetry axes parallel to the plane of projection

Table 3-7. Symmetry axes normal to the plane of projection

Symmetry axis or symmetry point	Graphical symbol	Screw vector of a right- handed screw axis in units of colorblind unit cell translation parallel to the axis	Printed symbol
Identity	None	None	1
Primed center of symmetry	0	None	1'
Primed center of symmetry and starred center of symmetry	•	None	Ī', Ī*
2-fold primed rotation axis		None	2'
2-fold primed screw axis	ý	1/2	21'
3-fold primed rotation axis		None	3'
3-fold primed screw axis		1/3	31'
3-fold primed screw axis		2/3	32'
4-fold primed rotation axis	•	None	4'
4-fold primed screw axis	$\mathbf{\mathbf{k}}$	1/4	41'
4-fold primed screw axis	•	2/4	42'
4-fold primed screw axis	\checkmark	3/4	43'
4-fold primed inversion	◆	None	4 '
6-fold primed rotation axis		None	6'
6-fold primed screw axis	1	1/6	61'
6-fold primed screw axis		2/6	<mark>6</mark> 2'
6-fold primed screw axis	<u>ا</u>	3/6	<mark>6</mark> 3'
6-fold primed screw axis		4/6	64'
6-fold primed screw axis		5/6	<mark>6</mark> 5'
6-bar primed inversion		None	<u></u> 6'

If a center of symmetry is on a rotation axes, the symbol of the center of 154 symmetry is placed onto the symbol of the rotation axis.

Table 3-8. Symmetry planes normal to the plane of projection

Symmetry plane	Graphical symbol	Glide vector in units of colorblind unit cell translation parallel to the projection plane	Printed symbol
Primed mirror plane		None	m'
Primed glide plane		1/2 lattice vector along line in projection plane	a', b', or c'
Primed glide plane		1/2 lattice vector normal to projection plane	a', b', or c'
Primed glide plane		One glide vector with two components: 1/2 along line parallel to projection plane, 1/2 normal to projection plane	n'
Primed glide plane and starred glide plane		Two glide vectors: 1/2 along line parallel to projection plane primed and 1/2 normal to projection plane starred	el' and e2*
Primed glide plane		1/4 along line parallel to projection plane, combined with 1/4 normal to projection plane (arrow indicates direction parallel to the projection plane for which the normal component is positive)	ď

Table 3-9. Symmetry planes parallel to the plane of projection

Symmetry plane	Graphical symbol	Glide vector in units of colorblind unit cell translation parallel to the projection plane	Printed symbol
Primed mirror plane		None	m'
Primed glide plane		1/2	a', b', or c'
Primed glide plane		One glide vector with two components, 1/2 in the direction of the arrow	n'
Primed glide plane and starred glide plane		Two glide vectors, 1/2 in either of the directions of the two arrows	e1' and e2*

Table 3-10. Symmetry axes inclined to the plane of projection (cubic groups only)

Symmetry axis	Graphical symbol	Screw vector of a right-handed screw axis in units of colorblind unit cell translation parallel to the axis	Printed symbol
2-fold primed rotation axis	• ¢ -\$ •	None	2'
2-fold primed screw axis	• •••	1/2	21'
3-fold primed rotation axis	× ×	None	3'
3-fold primed screw axis	XX	1/3	31'
3-fold primed screw axis	××	2/3	32'

Symmetry	Graphical symbol for planes normal to		Glide vector in units of colorblind unit cell translation for planes normal to		Printed	
plane	[011] and [011]	[101] and [101]	[011] and [011]	[101] and [101]	symbol	
Primed mirror plane			None	None	m'	
Primed glide plane			1/2 lattice vector along [100]	1/2 lattice vector along [010]	a' or b'	
Primed glide plane			1/2 lattice vector along [011] or along [011]	1/2 lattice vector along [101] or along [101]	a' or b'	
Primed glide plane And starred glide plane			Two glide vectors: 1/2 along [100] primed and 1/2 along [011] or along [011] starred	Two glide vectors: 1/2 along [010] primed and 1/2 along [101] or along [101] starred	el' and e2*	
Primed glide plane			One glide vector: 1/2 along [111] or along [111]	One glide vector: 1/2 along [111] or along [111]	n'	
Primed glide plane			1/2 along [111] or along [111]	1/2 along [111] or along [111]	d'	
Primed glide plane			1/2 along [111] or along [111]	1/2 along [111] or along [111]	d'	

Table 3-11. Symmetry planes inclined to the plane of projection (cubic groups only)



Table 3-12. Heights of symmetry operations above plane of projection

The text besides the symbols indicate the height of the symbols. x and y represent arbitrary heights.

Chapter 4

Rotation-reversal symmetry

This chapter summarizes some of the problems related to studying the concept of rotation-reversal symmetry as introduced by "Rotation-reversal symmetries in crystals and handed structures" by Gopalan & Litvin in their 2011 Nature Materials article¹. It will also discuss rotation-reversal symmetry concepts that were explored just prior to and in the early stages of developing distortion symmetry.

I will begin with some background on magnetic symmetry consequences for diffraction so that it may be compared to rotation-reversal symmetry in later sections. I am not an expert on diffraction, especially using neutron and electron sources, so this section represents my understanding of the phenomenon and should be accurate enough to convey the symmetry implications of interest here. Readers looking for detailed expert information on the subject should look elsewhere, especially the International Tables for Crystallography¹⁰¹.

4.1 Background on magnetic symmetry consequences for diffraction

There is an important consequence of magnetic symmetry that appears in the difference between x-ray diffraction, electron diffraction, and neutron diffraction. This consequence is an excellent example of the nature of how antisymmetry affects property prediction and will provide a concrete analogy for later discussions of rotation reversal symmetry.

The phenomenon of x-ray diffraction by crystals was discovered in the early part of the 20th century, creating a way to study matter at a very small scale. This remarkable phenomenon is caused by the collective effect of constructive and destructive interference of x-rays (photons) scattered by a regular arrangement of atoms in a crystal. By understanding this phenomenon, the internal arrangement of the atoms composing the crystal can by be found. Procedures for this are now routine.

X-ray diffraction can be described in a simple and elegant way by the Fourier transformation of the electron density of a crystal. Considering only x-ray intensity which is elastically scattered by electrons allows for the following equation:

Equation 1

$$I_{XRD}(\Delta \vec{k}) \propto \left| \int \rho_e(\vec{r}) \, e^{-2\pi i \vec{r} \cdot \Delta \vec{k}} \, d\vec{r} \right|^2$$

where $I_{XRD}(\Delta \vec{k})$ is the intensity of the diffracted beam at some wave vector difference between the incident and the diffracted beam $\Delta \vec{k}$. $\rho_e(\vec{r})$ is the electron density as a function of space \vec{r} . This equation does not require a crystal. It applies equally well in non-crystalline materials. However, consider that in the crystalline case the spatial distribution of electron density, $\rho_e(\vec{r})$, is periodic such that $\rho_e(\vec{r}) = \rho_e(\vec{r} + \vec{t})$ where \vec{t} is a lattice vector. In this case, an infinite crystal can be represented by a finite space which is mapped periodically. As such, it is only necessary to integrate Equation 1 over a finite unit

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cell, A. Furthermore, for a perfect infinite crystal, the intensity is zero for all $\Delta \vec{k}$ except those where $\Delta \vec{k} \cdot \vec{t} = 1$ for some $\vec{t} \in \Lambda$ where Λ is the set of all lattice vectors.

Equation 2

$$I_{XRD}(\Delta \vec{k}) \propto \begin{cases} \exists \vec{t} \in \Lambda : \Delta \vec{k} \cdot \vec{t} = 1, \qquad \left| \int_{A} \rho_{e}(\vec{r}) e^{-2\pi i \vec{r} \cdot \Delta \vec{k}} d\vec{r} \right|^{2} \\ else, \qquad 0 \end{cases}$$

Only a few decades before the discovery of x-ray diffraction and theoretical development thereof by Laue, Bragg, and others, the 230 crystallographic space groups were enumerated by Fedorov and Schönflies. The main idea of crystal symmetry is that there are transformations of space that when applied to a crystal leave everything about the crystal invariant. These transformations are symmetry operations of the crystal and together they form the crystal's space group. The major implication of this for understanding x-ray diffraction is that the electron density $\rho_e(\vec{r})$ in Equation 1 is a function of space and therefore must be invariant under the symmetry operations of the crystal, i.e. $\rho_e(\vec{r}) = \rho_e(a\vec{r} + \vec{t})$ where a is the linear component of the motion and \vec{t} is the translation component as discussed in Chapter 2 and Chapter 3. This idea generalizes the notion expressed in Equation 2 to an even smaller volume using spatial symmetry beyond just the periodic translation of a crystal.

The theory of x-ray diffraction as summarized above is an extremely successful theory in the physical sciences. Now consider how this concept is generalized to apply to neutron and electron diffraction. Unlike with x-rays, where scattering is approximately proportional to electron density, with neutrons and electrons we are not so lucky. In the case of x-rays, the only relevant interaction is electromagnetic interaction, as with all photons. Because of this, the scattering of x-rays is dominated by the crystal's electrons (nuclei being too heavy to contribute significantly in the frequency range of x-rays). The scattering of neutrons and electrons is generally much more complicated.

Unlike x-rays (photons), neutrons have magnetic moments and consequently can be scattered by magnetic fields in the crystal. This is interesting because (ignoring other complications, especially the nuclear scattering) it means that neutrons are sensitive to the spin polarization of electrons. With neutrons, the scattering power of this effect is proportional to the difference between "up" and "down" electrons: $f_{n^0}^{mag}(\vec{r}) \propto \rho_e^{\dagger}(\vec{r}) - \rho_e^{\downarrow}(\vec{r})$. This is in contrast to x-ray scattering where the scattering power is proportional to the sum: $f_{\gamma}(\vec{r}) \propto \rho_e(\vec{r}) = \rho_e^{\dagger}(\vec{r}) + \rho_e^{\downarrow}(\vec{r})$. Consequently, in a non-magnetic material, where $\rho_e^{\dagger}(\vec{r}) = \rho_e^{\dagger}(\vec{r})$, $f_{n^0}^{mag}(\vec{r}) = 0$. In a magnetic crystal, where $\rho_e^{\dagger}(\vec{r}) \neq \rho_e^{\downarrow}(\vec{r})$, $f_{n^0}^{mag}(\vec{r}) \neq 0$. This is where magnetic symmetry and the time reversal operation comes into play.



Figure 4-1. Antiferromagnetic MnF2¹²⁷.

Consider the example of antiferromagnetic (AF) MgF₂ illustrated in Figure 4-1. Ignoring the spins indicated by the red arrows, the space group of AF-MnF₂ is P4₂/mnm¹²⁸. Consider how the wave vector difference of $\Delta \vec{k} = (1\ 0\ 0)$ (in reciprocal lattice units) gives zero intensity in Equation 2. To keep things simple, let the scattering be represented by just the two Mn atom positions^v rather than the electron density:

Equation 3

^v The fluorine atoms are relevant too, but because the atomic number of Mn is much higher than F (Z_{Mn} =25 versus Z_F =9), using just the Mn atoms can be a crude approximation. The symmetry of MnF₂ does still cancel out the XRD intensity at (1 0 0) even with the F atoms, but Equation 3 is more complex.

$$I_{XRD}\left(\Delta \vec{k} = (1\ 0\ 0)\right) \propto \left| f_{\gamma}^{Mn\downarrow} e^{-2\pi i (0\ 0\ 0) \cdot (1\ 0\ 0)} + f_{\gamma}^{Mn\uparrow} e^{-2\pi i \left(\frac{1}{2}\frac{1}{2}\frac{1}{2}\right) \cdot (1\ 0\ 0)} \right|^2 = \left| f_{\gamma}^{Mn\downarrow} - f_{\gamma}^{Mn\uparrow} \right|^2$$

As previously mentioned, x-ray diffraction is insensitive to spin polarization, i.e. $f_{\gamma}^{Mn\downarrow} = f_{\gamma}^{Mn\uparrow}$. Therefore, $I_{XRD} (\Delta \vec{k} = (1 \ 0 \ 0)) = 0$. This is consistent with the reflection conditions given for P4₂/mnm, *i.e.* the sum of h, k, and I must be even for non-zero intensity at $\Delta \vec{k} = (h \ k \ I)^{101}$.

If neutron diffraction replaces x-ray diffraction and the same approximations and conditions are used, Equation 3 becomes:

Equation 4

$$I_{ND}\left(\Delta \vec{k} = (1 \ 0 \ 0)\right) \propto \left|f_{n^0}^{mag,Mn\downarrow} - f_{n^0}^{mag,Mn\uparrow}\right|^2$$

However, in the case of neutron scattering, opposite spins interact oppositely! Therefore, $f_{n^0}^{mag,Mn\downarrow} = -f_{n^0}^{mag,Mn\uparrow}$ and $I_{ND} (\Delta \vec{k} = (1 \ 0 \ 0)) \propto \left| 2 f_{n^0}^{mag,Mn\downarrow} \right|^2$. The non-zero intensity at (1 0 0) (see Figure 4-2) violates the reflection conditions given for P4₂/mnm! This is because P4₂/mnm is only the space group in a model for AF-MnF₂ which is "blind" to spin.



Figure 4-2. Neutron powder diffraction of AF-MnF₂ (source: www.cins.ca/docs/SS09/DHR_CNBC_June09.ppt).

Consider the 4₂ screw axis of P4₂/mnm located at ($\frac{1}{2}, 0, z$). This operation would take the Mn atom at (0,0,0) in Figure 4-1 to ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). This places a \downarrow spin on top of a \uparrow spin. We therefore should instead have this screw axis as a *primed* screw axis, 4₂', that is a screw axis followed by time reversal which switches \downarrow to \uparrow and vice versa. If we do this for all such operations of P4₂/mnm, we get the magnetic symmetry P4₂'/mnm'. This is 136.5.1156 in Litvin's magnetic space group tables¹⁰² and No. 1342 in the double antisymmetry space group listing. Interestingly, if we were to find the structure from neutron diffraction but not consider magnetic symmetry, we would have Pnnm type symmetry. This orthorhombic group would not be able to explain why the unit cell was perfectly tetragonal.

A primed operation acts on the spatial coordinates but also on the magnetic moments. With both the magnetic scattering of neutrons and x-ray scattering, the effect of a primed symmetry operation is fairly straightforward, i.e.

 $f_{n^0}^{mag}(\vec{r}) = -f_{n^0}^{mag}(a\vec{r} + \vec{t})$ and $f_{\gamma}(\vec{r}) = f_{\gamma}(a\vec{r} + \vec{t})$ respectively where a is the linear component of the motion and \vec{t} is the translation component of the primed symmetry operation. In the first case, time reversal, 1', reverses the sign of the property; in the second case, it does nothing. Unfortunately this is not the case with all properties. Sometimes the action of 1' may be more complicated. Consider the scattering of an electron by AF-MgF₂. The electron also interacts oppositely with opposite spin polarizations but the electrostatic repulsion is the same for \downarrow and \uparrow .

	Magnetic effect of spin polarized electron		Electrostatic effect of spin polarized electron		Net effect of
	1	\rightarrow	\uparrow	\rightarrow	I
X-ray diffraction (y)	0	0	+	+	No change
Neutron diffraction (n°)	+	-	0	0	Opposite
Electron diffraction (e-)	+	-	+	+	Complicated

Again, this is ignoring nuclear scattering in the neutron diffraction case and using magnetic scattering only.
4.2 Introduction to rotation-reversal symmetry

Rotation-reversal symmetry¹ was introduced to generalize the symmetry classification of crystals to include rotation reversal. The rotation-reversal operation, represented by 1^o was compared by analogy to the well-known time-reversal operation^{vi,vii}, represented by 1'. Rotation-reversal was meant to "reverse the sense of static rotations" of molecules or polyhedral units in crystals, e.g. the rotated BO₆ octahedra in a distorted ABO₃ perovskite. In the course of pursuing applications for rotation-reversal symmetry, it became clear that the "reversal of static rotations" concept was incomplete and ill-defined. It was formalized with the definitions given in Section 4.3. This work is unpublished, and thus also less refined than previous chapters, because it evolved into distortion symmetry. It has been included in this dissertation to both show the path that led to

^{vi} Rotation reversal has also been represented by 1* in two of our papers written prior to the development of distortion symmetry^{36,37}, now 1* refers specifically to distortion reversal, *i.e.* 1* : $\lambda \rightarrow -\lambda$, as discussed in Chapter 1.

^{vii} It is also worth noting that "time-reversal" is used in crystallography to reverse magnetic moments of magnetic atoms and not usually anything else. These magnetic moments are mostly due to the spins of unpaired electrons and so sometimes 1' may be described as "reversing spin". This notion of "time-reversal" may differ from those used elsewhere in the physical sciences.

developing distortion symmetry and also in case the concepts developed here ever find fitting applications.

From the original rotation-reversal symmetry paper:

"As 1^o reverses the sign of a mathematical cross product between two vectors (see Methods section), which is very common in describing physical quantities such as the curl of a vector field, it is applicable to a large number of physical properties."

This idea came from the concept of 1^o being applied to reverse all axial vectors. A key aspect of rotation-reversal symmetry as given by Gopalan & Litvin's original rotation-reversal symmetry paper is that 1^o reverses all "time-reversal invariant axial vectors". Although the concept was never developed in a sufficiently clear way and it is not certain whether it is even possible to develop it in a clear way that does not create contradictions, it is clear that if axial vectors and axial tensors (also known as pseudovectors and pseudotensors) are reversed, then cross-products between polar vectors and tensor products involving the Levi-Civita symbol should also be reversed otherwise contradictions will certainly exist. Because of the lack of clarity on this concept, this aspect of rotation-reversal symmetry is ignored by this chapter. The original rotationreversal symmetry paper also suggested that 1^o should reverse the direction that helices and spirals are wrapped (see Fig. 4 in the original rotation-reversal symmetry paper). The aspect of rotation-reversal symmetry is also ignored by this chapter due to a lack of clarity and apparent incompatibility with more prominent rotation-reversal symmetry ideas.

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4.3 Defining the rotation-reversal operation

Rotation reversal acts on rotated polyhedra, but "rotated polyhedra", and consequently the action of rotation reversal, are not sufficiently well defined. Since rotation-reversal symmetry was mostly described in how in supposedly applied to crystals, this section will focus on these definitions in crystals.

An atomic crystal will refer to a 3D-periodic set of atoms. For the purposes of this chapter, an *atom* is a pair of the form of (Z,**r**) where Z is an atomic species and **r** is the position of the atom (in Cartesian coordinates, i.e. $\mathbf{r} = (r_1, r_2, r_3)$). An *atomic species* is simply an atomic symbol, such as Ti. A polyhedral crystal is a 3D-periodic set of polyhedra. In this chapter, a polyhedra is a triple in the form of (**P**,**r**,**\omega**) where **P** is a polyhedra type, **x** is the position of the polyhedra (in Cartesian coordinates, i.e. $\mathbf{r} = (r_1, r_2, r_3)$), and **\omega** is the orientation vector or static rotation vector of the polyhedra (i.e. $\boldsymbol{\omega} = (\omega_1, \omega_2, \omega_3)$). A polyhedra type is a finite set of atoms, e.g. $\mathbf{P} = \{(Z_1, \mathbf{r}_1), (Z_2, \mathbf{r}_2), ..., (Z_n, \mathbf{r}_n)\}$.

Let p denote a function which maps polyhedral crystals to atomic crystals. Different polyhedral crystals can map to the same atomic crystal (i.e. p is surjective but not injective). Because of this, a well-defined inverse function does not exist (at least not without modifying the definition to allow for a set-valued function). This is why we have question 1 in Section 4.5. Polyhedral crystals which map to the same atomic crystal will be said to be *atomically* equivalent.

In this chapter, a symmetry element is a triple of the form $(\mathbf{a}, \mathbf{t}, c)$ where \mathbf{a} is a linear orthogonal transformation (i.e. a rotation matrix or improper rotation matrix), **t** is a Cartesian vector representing a translation, and c is either 1 or -1. If c is 1, the symmetry element is colorless. If c is -1, the symmetry element is said to be *rotation-reversing*. For those who are familiar with group representation theory, describing the operations of rotation-reversal symmetry in this way may make the connection to 1D real irreps very clear. For instance, if G is a rotation-reversal symmetry group then the function Γ : (**a**,**t**) \mapsto (c) for all (**a**,**t**,c) in G is a 1D real irrep of G's colorblind parent group, {(**a**,**t**) : (**a**,**t**,c) \in G}.

If we define a lattice basis for a crystal (atomic or polyhedral), we can use crystal coordinates in lieu of Cartesian coordinates. The relationship is given by $\mathbf{r} = \mathbf{x}\mathbf{\Lambda}$ where \mathbf{r} is in Cartesian coordinates, \mathbf{x} is in crystal coordinates, and $\mathbf{\Lambda}$ is a lattice basis expressed as a matrix.

Given an arbitrary polyhedral crystal $\mathbf{A} = \{(\mathbf{P}_1, \mathbf{r}_1, \boldsymbol{\omega}_1), \dots, (\mathbf{P}_n, \mathbf{r}_n, \boldsymbol{\omega}_n)\}, \rho(\mathbf{A})$ is the union of the sets of atoms of the polyhedra. We can express this as:

$$\rho(\mathbf{A}) = \bigcup_{i=1}^{n} \{ (Z, \mathbf{R}(\boldsymbol{\omega}_i)\mathbf{r}' + \mathbf{r}_i) : (Z, \mathbf{r}') \in \mathbf{P}_i \}$$

where $R(\omega)$ is the following rotation matrix:

 $\pmb{R}((\omega_1,\omega_2,\omega_3)) =$

 $\begin{pmatrix} 1 - 2\omega_2{}^2 - 2\omega_3{}^2 & 2\omega_1\omega_2 - 2\omega_3\sqrt{1 - \omega_1{}^2 - \omega_2{}^2 - \omega_3{}^2} & 2\omega_1\omega_3 + 2\omega_2\sqrt{1 - \omega_1{}^2 - \omega_2{}^2 - \omega_3{}^2} \\ 2\omega_1\omega_2 + 2\omega_3\sqrt{1 - \omega_1{}^2 - \omega_2{}^2 - \omega_3{}^2} & 1 - 2\omega_1{}^2 - 2\omega_3{}^2 & 2\omega_2\omega_3 - 2\omega_1\sqrt{1 - \omega_1{}^2 - \omega_2{}^2 - \omega_3{}^2} \\ 2\omega_1\omega_3 - 2\omega_2\sqrt{1 - \omega_1{}^2 - \omega_2{}^2 - \omega_3{}^2} & 2\omega_2\omega_3 + 2\omega_1\sqrt{1 - \omega_1{}^2 - \omega_2{}^2 - \omega_3{}^2} & 1 - 2\omega_1{}^2 - 2\omega_2{}^2 \end{pmatrix}$

This defines a rotation of $2\sin^{-1}\sqrt{\omega_1^2 + \omega_2^2 + \omega_3^2}$ around $(\omega_1, \omega_2, \omega_3)$. This definition works for rotations that are smaller than 90° in magnitude.

Note that relationship between the rotation vector, $\vec{\omega}$, and the rotation matrix, $R(\omega)$, is such that:

$$\frac{\boldsymbol{R}(\boldsymbol{\omega}) - \boldsymbol{R}(\boldsymbol{\omega})^{T}}{2} = \begin{pmatrix} 0 & -\omega_{z} & \omega_{y} \\ \omega_{z} & 0 & -\omega_{x} \\ -\omega_{y} & \omega_{x} & 0 \end{pmatrix}$$

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A symmetry element, (a,t,c), acts on a polyhedron, (P,r,ω) , such that:

$(a, \mathbf{t}, c)(\mathbf{P}, \mathbf{r}, \boldsymbol{\omega}) = (a\mathbf{P}, a\mathbf{r} + \mathbf{t}, c|a|a\boldsymbol{\omega})$

where |a| is the determinant of **a**. **aP** is the polyhedra type given by $aP = \{(Z, ar) : (Z, r) \in P\}$. Note that if **a** is a symmetry of the polyhedra type **P**, then **P** = **aP**. This often occurs in the rotation-reversal symmetry examples given by Gopalan and Litvin, e.g. arrays of squares that have 4° symmetry. This may account for some of the confusion about rotation-reversal symmetry. This definition of symmetry action on polyhedra is clearly not elegant, but it does seem to work and allows for static rotation vectors.

4.4 Examples of polyhedral crystals and their rotation-reversal symmetry

4.4.1 ABO₃ cubic perovskite example

ABO3 can be described with two types of polyhedra, A and BO3 where

 $A = \{(A, (0,0,0))\}$ $BO_3 = \{(B, (0,0,0)), (1/2O, (a_{BO},0,0)), (1/2O, (0,a_{BO},0)), (1/2O, (0,0, a_{BO})), (1/2O, (0,0, a_{BO})), (1/2O, (-a_{BO},0,0)), (1/2O, (0,-a_{BO},0,0)), (1/2O, (0,0,-a_{BO},0))\}$

where a_{BO} is the B-O bond distance. Here BO₃ has been defined with six $\frac{1}{2}$ oxygen atoms to form an octahedron but it could have instead been defined with the full oxygen atoms. The cubic perovskite structure can be expressed as a polyhedral crystal with Pm-3m1^o type symmetry. The lattice parameter is twice the B-O bond distance, i.e. $2a_{BO}$. The lattice basis, expressed in matrix form, is thus:

$$\Lambda_{cubic} = \begin{pmatrix} 2a_{BO} & 0 & 0\\ 0 & 2a_{BO} & 0\\ 0 & 0 & 2a_{BO} \end{pmatrix}$$

Listing just the polyhedra in the conventional unit cell (the volume defined by Λ_{cubic}), the cubic perovskite crystal is: {(**A**, (0,0,0), (0,0,0)), (**BO**₃, ($\frac{1}{2}$, $\frac{1}{2}$), (0,0,0))}. The positions have been given in crystal coordinates.

Note that the static rotation vectors are (0,0,0). This is required by the 1° symmetry. Pm-3m1° is given as number No. 1872 in the double antisymmetry space groups listing (although with * instead of °). The polyhedra positions above correspond to 1a and 1b Wyckoff positions listed for No. 1872. Note that the rotation vectors listed for those coordinates are [0,0,0]. This is consistent with the orientation vectors of the polyhedra.

4.4.2 ABO₃ a⁺a⁺c⁺ tilted perovskite example

The $a^+a^+c^+$ Glazer tilt pattern can be expressed as a polyhedral crystal with $I4^{\phi}/mmm^{\phi}$ type symmetry. The static rotation vectors of the **BO**₃ type polyhedra are (*a*,*a*,*c*). The lattice basis, expressed in matrix form, is:

$$\Lambda_{a^{+}a^{+}c^{+}} = 4a_{BO} \begin{pmatrix} 1 - 2a^{2} - 2c^{2} & 0 & 0\\ 0 & 1 - 2a^{2} - 2c^{2} & 0\\ 0 & 0 & 1 - 4a^{2} \end{pmatrix}$$

Listing just the symmetry unique polyhedra, the $a^+a^+c^+$ Glazer tilt pattern is: {(**A**,(0,0,0),(0,0,0)}, (**A**,(0,0,1/2),(0,0,0)}, (**A**,(0,1/2,0),(0,0,0)),(**BO**₃,(1/4,1/4),(a,a,c)</sub>)} I4^{ϕ}/mmm^{ϕ} is given as number No. 4206 in the double antisymmetry space group tables. The polyhedra positions above correspond to 2a, 2b, 4c, and 8f Wyckoff positions respectively:

Wyckoff	Translation unique polyhedra coordinates
2a	(A , (0,0,0), (0,0,0))
2b	(A , (0,0, ¹ / ₂), (0,0,0))
4c	(A , (0, ½, 0), (0, 0, 0))
	(A , (½,0,0), (0,0,0))
8f	(BO ₃ , (¹ / ₄ , ¹ / ₄), (<i>a</i> , <i>a</i> , <i>c</i>))
	(BO ₃ , (³ / ₄ , ³ / ₄ , ¹ / ₄), (-a, -a, c))
	(BO ₃ , (³ / ₄ , ¹ / ₄ , ¹ / ₄), (<i>a</i> , - <i>a</i> , - <i>c</i>))
	(BO ₃ , (¹ / ₄ , ³ / ₄ , ¹ / ₄), (-a, a, -c))

Note that these are consistent with the Wyckoff positions from the symmetry

listing as shown in Figure 4-3.



Figure 4-3. Symmetry diagram and Wyckoff positions (2a, 2b, 4c, and 8f) cropped from No. 4206 I4*/mmm* symmetry listing.

4.5 Problems with rotation-reversal symmetry

Given the definitions in Section 4.3, some of the questions we might ask are:

- How should an atomic crystal be partitioned into polyhedral units? Although we have a procedural way to create an atomic crystal from a polyhedral crystal (*i.e.* p as defined in Section 4.3), we do not have a procedural way of creating a polyhedral crystal from an atomic crystal. This is a serious problem because rotation-reversal symmetry operations cannot be applied to atomic crystals.
- 2. Can we derive property consequences for rotation-reversal symmetry that can be measured experimentally or calculated theoretically? An alternate question would be: How do different microscopic and macroscopic properties transform under these unconventional symmetry operations? Particularly, some properties may be "blind" to rotationreversal. For a property that is blind to rotation reversal, a rotation-reversal symmetry operation "looks the same" as a conventional symmetry operation, e.g. 4^Φ and 4. This idea comes from the analogy to magnetic symmetry where, for example, 4' symmetry would place the same restrictions on elastic stiffness as 4 symmetry, i.e. stiffness is "blind" to timereversal.
- 3. If bonds within polyhedra are perfectly rigid, are the property consequences of rotation-reversal symmetry exact? It may be that rotation-reversal symmetry property consequences will only hold approximately in real crystals but exactly with perfectly rigid polyhedra. It is not clear whether in a theoretical model with perfectly rigidly polyhedra property consequences would be exact.

4.6 Testing for symmetry in calculated elastic stiffness

Prof. Gopalan suggested that elastic stiffness may be blind to rotationreversal symmetry, just like with time-reversal symmetry (see question 2 in Section 4.5). This idea was tested using first-principles calculations in collaboration with James Rondinelli and Joshua Young. The results were inconclusive and have not been published.

The structure used to test this idea was SrTiO₃ with the a⁺a⁺c⁺ Glazer tilt pattern can be expressed as a polyhedral crystal with $I4^{\phi}/mmm^{\phi}$ type symmetry. This structure is not known to be stable experimentally, but this is not necessary for the first-principles calculation of elastic stiffness. The static rotation vector used was (0.204,0.204,0.408) corresponding to a 30° about [1,1,2]. The unit cell parameters were a=b=7.57660 Å, c=7.72272 Å, and a=β=γ=90°. The Wyckoff position of this polyhedral crystal were:

Wyckoff site	Polyhedron
1a	(Sr , (0,0,0), (0,0,0))
1b	(Sr , (0,0, ¹ / ₂), (0,0,0))
2c	(Sr , (0, ¹ / ₂ , 0), (0, 0, 0))
	$(Sr, (\frac{1}{2}, 0, 0), (0, 0, 0))$
4f	$(\text{TiO}_{3}, (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), (0.204, 0.204, 0.408))$
	$(TiO_3, (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}), (-0.204, -0.204, 0.408))$
	$(TiO_3, (\frac{3}{4}, \frac{1}{4}, \frac{1}{4}), (0.204, -0.204, -0.408))$
	$(\text{TiO}_{3}, (\frac{1}{4}, \frac{3}{4}, \frac{1}{4}), (-0.204, 0.204, -0.408))$

where $Sr = \{(Sr, (0,0,0))\}$ and $TiO_3 = \{(Ti, (0,0,0)), (\frac{1}{2}O, (2.5 \text{ Å},0,0)), (\frac{1}{2}O, (0,2.5 \text{ Å},0)), (\frac{1}{2}O, (0,0,2.5 \text{ Å})), (\frac{1}{2}O, (0,0$



Figure 4-4. SrTiO₃ with the $a^+a^+c^+$ Glazer tilt pattern.

Under the mapping p described in Section 4.3, the Wyckoff positions of the corresponding atomic crystal with Immm symmetry are:

Wyckoff site	Element	x	У	Z
2a	Sr	0	0	0
2b	Sr	0	0.5	0.5
2c	Sr	0.5	0.5	0
2d	Sr	0.5	0	0.5
8k	Ti	0.25	0.25	0.25
81	0	0	0.15117	0.30939
8m	0	0.32809	0	0.16598
8n	0	0.16436	0.31054	0

The macroscopic point group symmetry of this $a^+a^+c^+$ SrTiO₃ structure is 4^{Φ} /mmm^{Φ}. If the elastic stiffness was blind to 1^{Φ} as was suggested, then the calculated elastic constants should look like that of a crystal with 4/mmm symmetry rather than what the symmetry of the atomic crystal, mmm, would suggest. This should be correct if the elastic properties of a crystal are blind to the sign of the static rotation vectors in the same way the x-ray scattering is blind

to the spin polarization of an electron as discussed earlier in Section 4.1. This is to say that a polyhedron with \vec{w} rotation must "look" the same as a polyhedron with $-\vec{w}$ rotation when applying mechanical stress to the crystal. I was and am skeptical that this should be the case, but it is not clear to me that shouldn't. As discussed in Section 4.5, it may be that this symmetry only applies approximately or in the limit of perfectly rigid polyhedra. Note that the consequences of distortion symmetry discussed in Chapter 1 are exact and do not depend on rigidness or polyhedra of any kind.

For crystals with mmm the stiffness tensor in Voigt notation, C_{ij} , has nine independent coefficients: C_{11} , C_{12} , C_{13} , C_{22} , C_{23} , C_{33} , C_{44} , C_{55} , and C_{66} . Whereas for crystals with 4/mmm, it has only six: $C_{11}=C_{22}$, C_{12} , $C_{13}=C_{23}$, C_{33} , $C_{44}=C_{55}$, and C_{66} . Thus, if the elastic stiffness was blind to 1^{\oplus} as was suggested, the following differences should be zero for a structure with 4^{\oplus} /mmm^{\oplus} symmetry: $C_{11}-C_{22}$, C_{13} - C_{23} , and $C_{44}-C_{55}$. For a $a^{+}a^{+}c^{+}$ SrTiO₃ structure, the values calculated by Joshua Young and James Rondinelli using VASP were:

C₁₁ - C₂₂ = -0.02 GPa C₁₃ - C₂₃ = -0.01GPa

C₄₄ - C₅₅ = 0.72GPa

These differences are fairly small, but the third is large enough to make the conclusion unclear. Also, from subsequent communication with Joshua Young and James Rondinelli, it seems that the structure they used did not perfectly match the a⁺a⁺c⁺ SrTiO₃ structure given in this section. Further elastic stiffness calculations that I performed on this and other structures in Materials Studio using

the CASTEP module showed that when symmetry was disabled, such that the software did not automatically symmetrize the results to be consistent with the conventional symmetry, there were significant deviations from the conventional symmetry. This is clearly a problem for testing the consequences of rotation-reversal symmetry, because it means that the methods are not accurate enough to clearly show even the conventional symmetry.



4.7 On applying rotation-reversal symmetry to electron density

Figure 4-5. Calculated electron density of SrTiO3 with the a+a+c+ Glazer tilt pattern.

Cross-sections for left and right contour plots are the equatorial plane indicated by the thick black line on the TiO_3 octahedra highlighted with blue and red respectively.

Another aspect of rotation-reversal symmetry that was not addressed by Gopalan & Litvin's original work¹ on the subject how to apply it to a continuous structure like the electron density of a crystal. In Figure 4-5, the top two images are contour plot cross-sections of calculated electron density in a⁺a⁺c⁺ SrTiO₃. The black squares are the edges of the TiO₃ octahedra. The corresponding locations are given by the thick black lines in the bottom images.

The top right is a mirror image of left; this is a consequence of the conventional mmm symmetry enforced by the simulation software (VASP). With the rotation-reversal symmetry of the polyhedral crystal description of $a^+a^+c^+$ SrTiO₃ given in the previous section, $14^{\circ}/mmm^{\circ}$, these two octahedra are related by 4° .

The most obvious way to generalize the ideas presented in Section 4.3 to apply to electron density is to allow the electron density to be part of the polyhedra. In Figure 4-5, the square on the left and its contents can be mirrored into the square on the right, as is consistent with the conventional symmetry of this structure. 4° also relates these two squares, but if the contents are literally cut and pasted, they do not match (see that the "triangular" contour lines point in opposite directions around the squares). So, either this $a^+a^+c^+$ SrTiO₃ structure that was given as a prime example of rotation-reversal symmetry does not actually have rotation-reversal symmetry when calculated electron density is considered or we cannot simply just cut-and-paste in this way. This raises the question of how electron density may by decomposed into polyhedra. This

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question is essentially just a more complicated variation of question 1 from Section 4.5.

4.8 Final remarks on rotation-reversal symmetry and polyhedral crystals

As seen in Section 4.3, the description of polyhedral crystals is considerably more complicated than the conventional description of atomic crystals because it adds polyhedral types, static rotation vectors, and a complicated definition of action of symmetry operations. It is further complicated by the consideration of electron density as discussed in Section 4.7 whereas with conventional symmetry, application to electron density flows naturally from how symmetry is applied to discrete atomic positions. It is my opinion that these complicated mechanisms are necessary in order to make the notion of rotation-reversal symmetry sufficiently precise. I also note that it is much simpler to describe distortions and distortion symmetry (see Chapter 1) than it is to describe polyhedral crystals and rotation-reversal symmetry. Symmetry consequences and application to electron density for distortion symmetry is very clear and straight-forward. The complications of the definitions (Section 4.3), the problems and unanswered questions (Section 4.5 and 4.7), and the problems with testing the suggested consequences of rotation-reversal symmetry (Section 4.6) all helped motivate the development of distortion symmetry.

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