UNDERSTANDING THE PHOTOREFRACTIVE EFFECT BY CRYSTAL GROUP THEORY

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Introduction

The photorefractive effect is a nonlinear optic phenomenon present in some optically active crystals. It entails the photorefractive index of the material changing when photons excite valence electrons to the conduction band. An alternative perspective is to examine the bond changes in the crystal, rather than the carriers, as the cause of the change. One method to examine the bond structure is to study the crystal structure using group theory to understand the symmetries present in the crystal. To that end, this paper will explain the basics of crystal physics, symmetry, group theory, and group representation to find mathematical solutions to explain how electromagnetic waves (light) propagate through the crystal. Finally, this paper will reflect on the experiment that inspired this investigation, and consider whether these methods can explain the phenomena observed.

In reading this paper, it would be useful to have some background in set theory, linear algebra, and differential equations. Some theorems from these subjects will be stated explicitly, with references in the bibliography, but the list will not be exhaustive. It may also be helpful to have experience in semiconductor or quantum physics. This paper will strive to cater to a mathematical background, but familiarity with subjects such as electron absorption, energy levels, and quantum states will be assumed. With that in mind, let us begin with some physical concepts.

Crystals

The most natural starting point to examine the photorefractive effect is by defining a *crystal* as a highly ordered array of atoms. Ideally, this array would be spatially infinite. Far from the edges and on the atomic scale, it will be approximated as such. It would also perfectly spatially repeat in all directions. This spatial symmetry is usually captured by the *unit cell*, a section of the crystal that can be spatially repeated to reproduce the whole. More useful, however, is the *primitive unit cell*, a unit cell that ;'contains the least number of atoms that can still reproduce the entire regular structure of the crystal. This unit cell is useful precisely because of its normalization.

Symmetries

All unit cells will have certain symmetries; that is, bijections from $\mathbb{R}^3$ to $\mathbb{R}^3$ that map unit cells into unit cells. However, we will consider them as acting on the unit cell, and by extension, the crystal lattice. They will map all lattice points to other lattice points, all sides to other sides, et cetera, so that the transformed unit cell is precisely indistinguishable from the original. This set of transformations will be called the point group of the crystal. It can essentially be split into two types of operation: flips and rotations. Flips will act across symmetry planes, such as a plane perpendicular to the face of a cube, or the plane passing through two corners of a tetrahedron. Rotations will similarly act about an axis of rotation, such as a line passing through the corner of a tetrahedron, or perpendicular through the midpoint of a cube face. In studying crystal group theory, it has been shown that there are only fourteen such point groups.

Figure 1, The Point Group Symmetries of a Cube

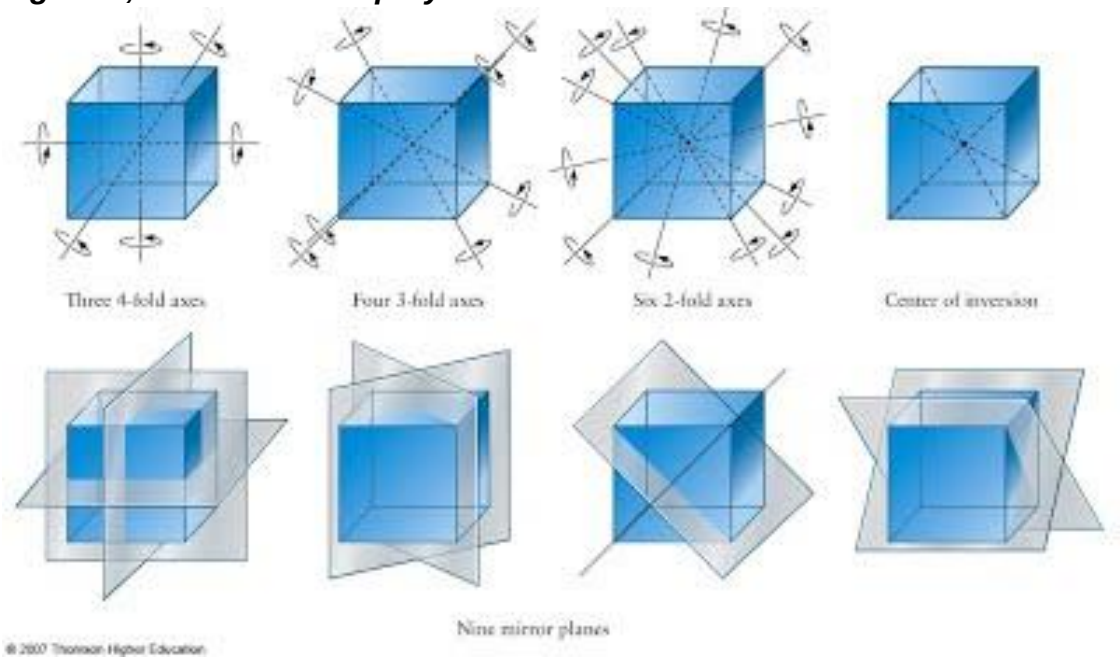
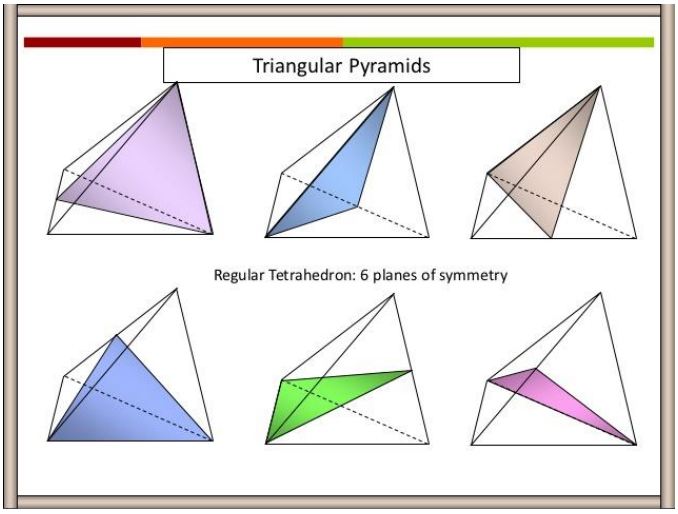
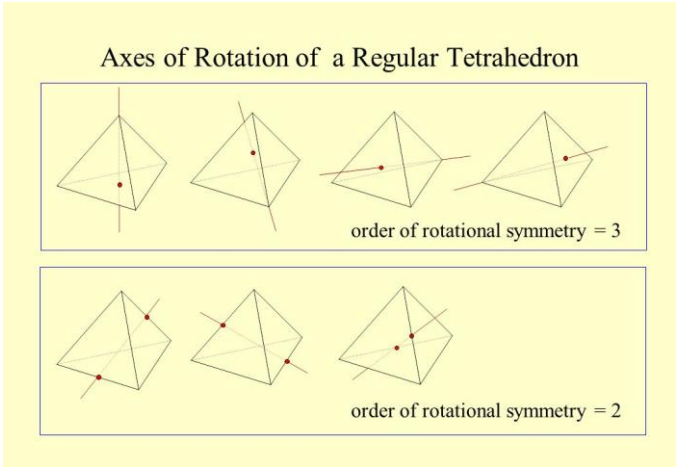


Figure 2, The Point Group Symmetries of the Tetrahedron

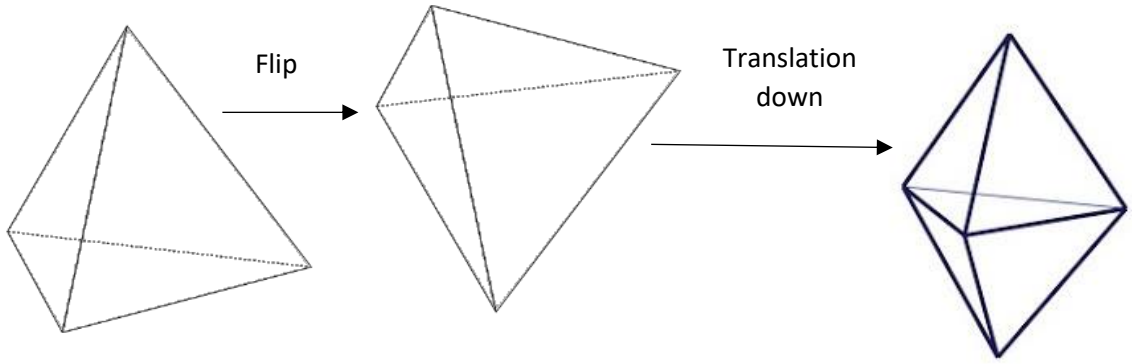




The other important consideration of crystal symmetry is that of space group symmetry. Space group symmetry might wrongly be understood as the symmetry of a unit cell that is allowed to translate as it undergoes a point group operation. However, this designation is misleading, as some operations allowed by space groups due to the translations would not be allowed by the point group; these are called *non-symmorphic* operations. For instance, flipping a tetrahedron across its mid-plane is not allowed in the point group, as it flips the unit cell upside down. However, if we do so and then translate the unit cell down a lattice length, it might fit into the lattice. Thus, this operation would be part of a space group for some tetrahedral crystals, despite the fact that its non-translation part is not in the point group. However, space groups do share some

similarity to the point groups in that they too can be split into two categories—the screw axis symmetries, which combine a rotation about an axis with a translation along a potentially different axis, and the glide symmetries, which combine a flip across a symmetry plane with a linear translation. Once we understand the unit cell structure of our crystal, it is important to verify the space group designation. It has been shown that there are two hundred thirty space groups while there are only fourteen point groups[1]; thus, assuming that the space group is merely translations combined with the members of the point group could be a serious mistake.

Figure 3, Demonstrating a Non-symmorphic Tetrahedral Space Group Operation



Group Theory

We have previously described the elements of the point symmetry *group*. We will now detail the meaning and usefulness of this term, in addition to why the symmetry operations form a group. In simplest terms, a group is a mathematical set with an operation defined on it as "multiplication" with certain properties. The "product" of any two elements in the set must be in the set, i.e. the operation must be closed. Every element in the set must have a unique multiplicative inverse in the set. The multiplication has to be associative, meaning that for any three elements x,y,z in the group, $x * (y * z) = (x * y) * z$. There must also exist an identity, denoted 1_G or e, in the group so that for every element in the group, x, the identity acts so that $e * x = x * e = x$. Note that the multiplication does not have to be commutative. In symmetry groups, the multiplication operation is the composition of the transformations.

Let us consider as examples Sym(3), the symmetric group on three elements, and D_3, the dihedral group of three elements or the symmetries of the equilateral triangle. As a set, Sym(3) can be considered the set of permutations on three letters and represented as (), which keeps all three points in their current spots; (12) which switches 1 and 2; (13) and (23) in similar fashion; (123) which sends 1 to 2, 2 to 3 and 3 to 1; and (132) which acts similarly. This multiplication table follows. Note that the permutations of order 3 (that is (123) and (132)) and the identity form a subgroup.

[1] (Bradley and Cracknell 2009)

Table 1, Multiplication Table for S_3

	()	**(12)**	**(13)**	**(23)**	**(123)**	**(132)**
()	()	(12)	(13)	(23)	(123)	(132)
(12)	(12)	()	(123)	(132)	(13)	(23)
(13)	(13)	(132)	()	(123)	(23)	(12)
(23)	(23)	(123)	(132)	()	(12)	(13)
(123)	(123)	(23)	(12)	(13)	(132)	()
(132)	(132)	(13)	(23)	(12)	()	(123)

Our identity will be (), because it doesn't change anything. For all the permutations of length two, the inverses will be themselves; for the permutations of length 3, it will be the other one. This group is closed because the product of any two elements is an element of the group. It can be observed from the multiplication table that the set {(), (123), (132)} is a subgroup because it is also closed and contains the identity. There are also three subgroups of size two: {(),(12)},{(),(13)}, and {(),(23)}. Associativity is true for all permutation groups, but not easy to prove except by brute force. The following multiplication tables demonstrate associativity by brute force.

Table 2, Association Table for S_3

	()	**(12)**	**(13)**	**(23)**	**(123)**	**(132)**
()()	()	(12)	(13)	(23)	(123)	(132)
(12)()	(12)	()	(123)	(132)	(13)	(23)
(13)()	(13)	(132)	()	(123)	(23)	(12)
(23)()	(23)	(123)	(132)	()	(12)	(13)
(123)()	(123)	(23)	(12)	(13)	(132)	()
(132)()	(132)	(13)	(23)	(12)	()	(123)
	()()	**()(12)**	**()(13)**	**()(23)**	**()(123)**	**()(132)**
()	()	(12)	(13)	(23)	(123)	(132)
(12)	(12)	()	(123)	(132)	(13)	(23)
(13)	(13)	(132)	()	(123)	(23)	(12)
(23)	(23)	(123)	(132)	()	(12)	(13)
(123)	(123)	(23)	(12)	(13)	(132)	()
(132)	(132)	(13)	(23)	(12)	()	(123)

	()	**(12)**	**(13)**	**(23)**	**(123)**	**(132)**
()(12)	(12)	()	(123)	(132)	(13)	(23)
(12)(12)	()	(12)	(13)	(23)	(123)	(132)
(13)(12)	(132)	(13)	(23)	(12)	()	(123)
(23)(12)	(123)	(23)	(12)	(13)	(132)	()
(123)(12)	(23)	(123)	(132)	()	(12)	(13)
(132)(12)	(13)	(132)	()	(123)	(23)	(12)
	(12)()	**(12)(12)**	**(12)(13)**	**(12)(23)**	**(12)(123)**	**(12)(132)**
()	(12)	()	(123)	(132)	(13)	(23)
(12)	()	(12)	(13)	(23)	(123)	(132)
(13)	(132)	(13)	(23)	(12)	()	(123)
(23)	(123)	(23)	(12)	(13)	(132)	()
(123)	(23)	(123)	(132)	()	(12)	(13)
(132)	(13)	(132)	()	(123)	(23)	(12)

	()	**(12)**	**(13)**	**(23)**	**(123)**	**(132)**
()(13)	(13)	(132)	()	(123)	(23)	(12)
(12)(13)	(123)	(23)	(12)	(13)	(132)	()
(13)(13)	()	(12)	(13)	(23)	(123)	(132)
(23)(13)	(132)	(13)	(23)	(12)	()	(123)
(123)(13)	(12)	()	(123)	(132)	(13)	(23)
(132)(13)	(23)	(123)	(132)	()	(12)	(13)
	(13)()	**(13)(12)**	**(13)(13)**	**(13)(23)**	**(13)(123)**	**(13)(132)**
()	(13)	(132)	()	(123)	(23)	(12)
(12)	(123)	(23)	(12)	(13)	(132)	()
(13)	()	(12)	(13)	(23)	(123)	(132)
(23)	(132)	(13)	(23)	(12)	()	(123)
(123)	(12)	()	(123)	(132)	(13)	(23)
(132)	(23)	(123)	(132)	()	(12)	(13)

	()	**(12)**	**(13)**	**(23)**	**(123)**	**(132)**
()(23)	(23)	(123)	(132)	()	(12)	(13)
(12)(23)	(132)	(13)	(23)	(12)	()	(123)
(13)(23)	(123)	(23)	(12)	(13)	(132)	()
(23)(23)	()	(12)	(13)	(23)	(123)	(132)
(123)(23)	(13)	(132)	()	(123)	(23)	(12)
(132)(23)	(12)	()	(123)	(132)	(13)	(23)
	(23)()	**(23)(12)**	**(23)(13)**	**(23)(23)**	**(23)(123)**	**(23)(132)**
()	(23)	(123)	(132)	()	(12)	(13)
(12)	(132)	(13)	(23)	(12)	()	(123)
(13)	(123)	(23)	(12)	(13)	(132)	()
(23)	()	(12)	(13)	(23)	(123)	(132)
(123)	(13)	(132)	()	(123)	(23)	(12)
(132)	(12)	()	(123)	(132)	(13)	(23)

	()	**(12)**	**(13)**	**(23)**	**(123)**	**(132)**
()(123)	(123)	(23)	(12)	(13)	(132)	()
(12)(123)	(13)	(132)	()	(123)	(23)	(12)
(13)(123)	(23)	(123)	(132)	()	(12)	(13)
(23)(123)	(12)	()	(123)	(132)	(13)	(23)
(123)(123)	(132)	(13)	(23)	(12)	()	(123)
(132)(123)	()	(12)	(13)	(23)	(123)	(132)
	(123)()	**(123)(12)**	**(123)(13)**	**(123)(23)**	**(123)(123)**	**(123)(132)**
()	(123)	(23)	(12)	(13)	(132)	()
(12)	(13)	(132)	()	(123)	(23)	(12)
(13)	(23)	(123)	(132)	()	(12)	(13)
(23)	(12)	()	(123)	(132)	(13)	(23)
(123)	(132)	(13)	(23)	(12)	()	(123)
(132)	()	(12)	(13)	(23)	(123)	(132)

	()	**(12)**	**(13)**	**(23)**	**(123)**	**(132)**
()(132)	(132)	(13)	(23)	(12)	()	(123)
(12)(132)	(23)	(123)	(132)	()	(12)	(13)
(13)(132)	(12)	()	(123)	(132)	(13)	(23)
(23)(132)	(13)	(132)	()	(123)	(23)	(12)
(123)(132)	()	(12)	(13)	(23)	(123)	(132)
(132)(132)	(123)	(23)	(12)	(13)	(132)	()
	(132)()	**(132)(12)**	**(132)(13)**	**(132)(23)**	**(132)(123)**	**(132)(132)**
()	(132)	(13)	(23)	(12)	()	(123)
(12)	(23)	(123)	(132)	()	(12)	(13)
(13)	(12)	()	(123)	(132)	(13)	(23)
(23)	(13)	(132)	()	(123)	(23)	(12)
(123)	()	(12)	(13)	(23)	(123)	(132)
(132)	(123)	(23)	(12)	(13)	(132)	()

For D_3, the symmetries of the regular 3-gon (i.e. equilateral triangle), we get the elements C_0, C_{120}, C_{240}, (rotations by 0, 120, or 240°) r_1, r_2, and r_3 (flips across the line defined by r_n and the midpoint of the opposite side). C_0 is our identity, because it leaves all points of the triangle as is. C_{120} and C_{240} will be inverses, because they will rotate the triangle by 360° back to C_0. Similarly, r_1, r_2, and r_3 will be their own inverses, because they can just be flipped back. Again, associativity is hard to prove except by brute force as we did with Sym(3). Instead, we will show in the next section that D_3 is naturally equivalent to another group for which association follows naturally from the definition of multiplication; the existence of this equivalence is enough to show that D_3 is associative as well. In comparison, closure is easy to understand by simply looking at the multiplication table for this group.

Table 3, Multiplication Table for D_3

	C_0	**C_{120}**	**C_{240}**	**r_1**	**r_2**	**r_3**
C_0	C_0	C_{120}	C_{240}	r_1	r_2	r_3
C_{120}	C_{120}	C_{240}	C_0	r_2	r_3	r_1
C_{240}	C_{240}	C_0	C_{120}	r_3	r_1	r_2
r_1	r_1	r_3	r_2	C_0	C_{240}	C_{120}
r_2	r_2	r_1	r_3	C_{120}	C_0	C_{240}
r_3	r_3	r_2	r_1	C_{240}	C_{120}	C_0

As you can see, the rotations in this group form a subgroup, because every element has an inverse, and the subgroup is closed. There are also three subgroups of size two: {r_1, C_0}, {r_2, C_0}, and {r_3, C_0}.

Turning the point symmetries of a crystal into a group allows us to apply our symmetry operations on the crystal unit cell, and to each other, in a sensible way that relates the operations to each other more clearly. It can also give us a sense of the properties of the group elements. One property is *element order* (how many times an element of a finite group must be performed to return to the identity). Another is the presence of *subgroups* (a subset of elements whose products are closed and have inverses within the subset). Finally, the *fixed points* and *orbits* of a finite group element, defined as follows, are two useful concepts for determining the properties of a group.

$$X^g = \{x \in G | g * x = x\} \, for \; g \in G \text{ (Eq. 1)}$$

$$G * x = \{g * x | g \in G\} for \; x \in X, the \; set \; G \; acts \; on \text{ (Eq. 2)}$$

For us, X will be the lattice points of the unit cell. The point group will be the set of point symmetries operated on by composition, where the elements act on the set in a defined order.

Group Representations

Now that the elements of the point symmetry operations have been translated into a group like D_3, it would be helpful to create another representation for them. This representation will mathematically describe the group in a way that highlights certain properties. We will construct our representation by creating a mapping from the original group to a set of nonsingular matrices, i.e. matrices with nonzero determinants, and thus matrices with matrix inverses.

A mapping is a function that pairs the elements of two sets. We want the mapping to preserve the multiplication structure of the group—this type of mapping is called a (group) *homomorphism*, i.e.

$$f(g_1 * g_2) = f(g_1) * f(g_2) \text{ (Eq. 3)}$$

Homomorphisms can also associate non-matrix groups with each other. For instance, we can construct a special function between Sym(3) and D_3 to prove D_3 is associative. This *isomorphism* needs to be a surjective and injective (onto and one to one) homomorphism. It happens that a bijective homomorphism between two groups that are the same size will be an isomorphism. We then define an equivalence relation, ~, to be a relation on a set, S, that is reflexive, i.e.

$$a \sim a, \forall a \in S \quad \text{(Eq. 4)}$$

symmetric, i.e.

$$a \sim b \rightarrow b \sim a, \forall a, b \in S \qquad \text{(Eq. 5)}$$

and transitive, i.e.

$$(a \sim b \; and \; b \sim c) \rightarrow a \sim c, \forall a, b, c \in S \qquad \text{(Eq. 6)}$$

In some ways, the equivalence relation represents equality within the set. It is known that an isomorphism between two groups defines an equivalence relation between the two groups. In the language of representation, two groups related by an equivalence relation are isomorphic, and thus faithfully represented by the other—that is, if one has three subgroups of size two or an associative multiplication, the other does as well.

We can construct an isomorphism between the two earlier groups as follows. Notice that the multiplication table for each element matches up as required for a homomorphism.

$C_0 \rightarrow$ ()
$r_3 \rightarrow$ (12)
$r_2 \rightarrow$ (13)
$r_1 \rightarrow$ (23)
$C_{120} \rightarrow$ (123)
$C_{240} \rightarrow$ (132)

For abstract groups such as our symmetry groups, it is useful to construct an isomorphism from our group into the nonsingular matrices with matrix multiplication as the group operation. It is a simple application of the definition of a group to show the invertible matrices are a group. Thus, any closed subset of the invertible matrices with a complete set of element inverses (i.e. subgroup) is a group itself.

For our purposes, we are interested in matrices that act on a finite-dimensional complex vector space. It is worth noting that a vector space is a group on which the multiplication is defined as “addition” and a “scalar multiplication” for elements exists. Similar to a group, it must be closed, associative, and have a unique identity for each operation. In addition, the “addition” must be commutative, the addition must have inverses in the set, and the operations must distribute across each other. The vector space will initially be the same dimension as the number of symmetry operations and complex so that we can allow for quantum mechanical solutions.

We can make many possible homomorphisms between two groups, not all of which are isomorphisms. One such mapping from a group to a matrix group will be the trivial mapping, which sends all elements of the group to the identity matrix. But we will be most interested in the irreducible representations. These representations have only trivial *invariant subspaces*; that is, subspaces, W, so that under a representation, R:

$$\forall w \in W, R(w) \in W \text{ (Eq. 7)}$$

A subspace is a vector space that is a subset of another vector space with the same “addition” and “scalar multiplication”. The trivial subspaces are the vector space and the zero vector. If a representation has a nontrivial invariant subspace, then the representation essentially splits into two matrices and can be represented as block matrix.

Proving that the vector space the representation operates on only has trivial invariant subspaces can be a tedious process, so we will apply a form of Burnside's Lemma to the matrix group instead. The original form of Burnside's Lemma relates the number of unique orbits, denoted X(G), and the fixed points of a group. Take |G| to be the size of G, that is, the number of elements in G.

$$X(G) = \frac{1}{|G|} * \sum_{g \in G} |X^g| \qquad \text{(Eq. 8)}$$

But this definition has an even simpler form for matrix groups. Take our group to be denoted G, and the elements within to be G_i. Let $\gamma: G \rightarrow GL(n,\mathbb{C})$ be the representation. The set $GL(n,\mathbb{C})$ is the set of the invertible matrices with complex entries. Define the function χ_γ, the character of the representation defined by homomorphism γ, to be the trace of the matrix $\gamma(G_i)$ for each G_i in the group G. We can then say

$$\frac{1}{|G|}\sum_{i=1}^{|G|} \left|\chi_\gamma(G_i)\right|^2 = 1 \qquad \text{(Eq. 9)}$$

if and only if the representation is irreducible. As an example, look at the matrix representation of D_3 or Sym(3). This is the isomorphism between D_3 and permutations of the identity matrix.

$$C_0 \rightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$r_3 \rightarrow \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$r_2 \rightarrow \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$r_1 \rightarrow \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}$$

$$C_{120} \rightarrow \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix}$$

$$C_{240} \rightarrow \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}$$

It is a straight forward calculation to compute that:

$$\sum_{i=1}^{|G|} \left|\chi_\gamma(G)\right|^2 = \begin{array}{l} \left|\chi_\gamma(())\right|^2 + \left|\chi_\gamma((123))\right|^2 + \left|\chi_\gamma((132))\right|^2 \\ +\left|\chi_\gamma((12))\right|^2 + \left|\chi_\gamma((13))\right|^2 + \left|\chi_\gamma((23))\right|^2 \end{array} \qquad \text{(Eq. 10)}$$

$$\sum_{i=1}^{|G|} \left|\chi_\gamma(G)\right|^2 = (9 + 0 + 0 + 1 + 1 + 1) = 12 \qquad \text{(Eq. 11)}$$

Since the sum isn't six, the size of D_3, this representation is reducible. Thus, the elements γ(Gi) have nontrivial invariant subspaces, each of the flips can be viewed as block matrix. Instead, let's try the following irreducible representation.

$$() \rightarrow \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \chi = 2$$

$$(12) \rightarrow \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \chi = 0$$

$$(13) \rightarrow \begin{bmatrix} 0 & e^{-\frac{2\pi i}{3}} \\ e^{\frac{2\pi i}{3}} & 0 \end{bmatrix}, \chi = 0$$

$$(23) \rightarrow \begin{bmatrix} 0 & e^{\frac{2\pi i}{3}} \\ e^{-\frac{2\pi i}{3}} & 0 \end{bmatrix}, \chi = 0$$

$$(123) \rightarrow \begin{bmatrix} e^{\frac{2\pi i}{3}} & 0 \\ 0 & e^{-\frac{2\pi i}{3}} \end{bmatrix}, \chi = -1$$

$$(132) \rightarrow \begin{bmatrix} e^{-\frac{2\pi i}{3}} & 0 \\ 0 & e^{\frac{2\pi i}{3}} \end{bmatrix}, \chi = -1$$

Let's check that it is irreducible.

$$\frac{1}{|G|}\sum_{i=1}^{|G|} \left|\chi_\gamma(\mathrm{G})\right|^2 = \frac{1}{6} * (4 + 0 + 0 + 0 + 1 + 1) = 1 \qquad \text{(Eq. 12)}$$

This one is irreducible.

Once we find an irreducible representation, there are two standard ways to denote the representation: Mulliken and active notation. Mulliken notation represents a group by the symmetries it represents. For instance, rotational symmetries about a principal axis are denoted by A. This notation uses different letters (A, B, T, etc.) to represent the different types of symmetry (singly degenerate symmetric rotation, singly degenerate anti-symmetric rotation, and triply degenerate, respectively[2]). However, if multiple operations take advantage of the same symmetry, the symmetry is degenerate. The operations are then denoted by adding numbered subscripts to the letters representing the symmetries. This can be unnecessarily confusing to an inexperienced reader. Additionally, this representation still uses composition as its "multiplication," which is not a particularly intuitive operation. Therefore, we will not be using this representation.

Instead, we will be using the active notation, which represents the group elements by how they transform the points of a unit cell; it can be compared to the dihedral group for a polygon (and by extension, the associated symmetry group) by representing the unit cell as a polygon. This has the advantage that every operation is uniquely assigned to a matrix, eliminating notation degeneracy. In addition, because we are using matrices as our group elements, we can use matrix multiplication as our multiplication. This, in addition to being more intuitive, eliminates most of the work to prove the representation is a group with associativity, inverses, an identity, and closure, because many of those properties are allowed to descend from the properties of matrix multiplication. If we move to unitary matrices, that is matrices which have a conjugate transpose equal to their inverse

$$M \; so \; that \; MM^\dagger = M\overline{M^T} = M\bar{M}^T = 1 = M^\dagger M \text{ (Eq. 13)}$$

[2] http://mathworld.wolfram.com/MullikenSymbols.html

then we will additionally have a set of group elements that do not change the size or angles of the unit cell, making them true point group operations.

The space groups can also be represented by matrices. Some of them will still be the point group operations. Some will have translation matrices, where the whole unit cell is moved by whole or fractional unit lengths, added on to them. Some will be translations combined with matrices for operations that were not present in the point group. In any case, these operations also will not change the size of the unit cell, meaning that they, too, will be normalized operations. However, it is worth noting that every point group will have multiple space groups associated with it, and not every space group will contain all the elements of the point group or all the non-point group operations. This is when it becomes helpful to study not only the unit cell, but also the entire crystalline structure to gain some insight as to which of the many space groups may contain the appropriate operations.

Symmetry-Adapted Functions

Only some functions will be able to fulfill the constraints required by crystal symmetry. These waves also need to be general enough to be constrained to fit the properties of many different types of waves, such as magnetic, acoustic, or photonic. To do so, it must satisfy the wave equation.

$$\Delta f - \frac{d^2 f}{dt^2} = 0 \text{ (Eq. 14)}$$

This multidimensional partial differential equation will need many constraints to give a unique solution. Some of these constraints will come from modeling the crystal as infinite, others from the type of wave. But the majority of the constraints will be taken from the elements of the symmetry matrix group. Therefore, we will find a general solution to the equation, and apply the elements of the symmetry group to it until we develop a particular solution.

The most general form these symmetric functions can take in three-dimensional space involves the spherical harmonic functions. These act somewhat similarly to the trigonometric functions of the Fourier series in one dimension, but can take in more constraints and act spatially, not linearly. They can be transformed into an infinite sum that allows them to meet many different types of wave and boundary conditions.

In their general form, the spherical harmonics are as follows:

$$Y_l^m(\theta, \varphi) = \sqrt{\frac{(2l+1)*(l-|m|)!}{4\pi*(l+|m|)!}} * P_l^m(\cos(\theta)) * \mathrm{e}^{i*m*\phi} \text{(Eq. 15)}$$

where P_l^m is the associated Legendre Polynomial, which is defined as:

$$P_l^m = \frac{1}{2^l * l!} * (\sin(\theta))^{|m|} * \frac{d^{l+|m|}}{d\cos(\theta)^{l+|m|}} ((\cos(\theta))^2 - 1)^l \text{ (Eq. 16)}$$

However, when we use these in a Fourier-type summation, we need the sum as a whole to satisfy the required symmetries. We can ensure this by following the process outlined in Bradley and Cracknell's *Mathematical Theory of Symmetry in Solids: Representation Theory for Point Groups and Space Groups*. This process involves

finding the three angles of rotation, α, β, and γ, that describe the point group operations. One then constructs a *group ring*, which is a group that has an addition defined on it. Using theorems about such a structure, we can define all bases for the vector space. We can then associate these bases to representations of the group. Summing over all group elements, we can derive the symmetry-adapted functions that form a basis for the representation. The elements of the group ring, W, can then operate on the symmetric functions as follows, with D^i as the ith representation, and C and d as certain constants.

$$W_{t,s}^{i} * Y_l^m(\theta,\varphi) = \frac{d_i}{|G|}\sum_{R\in G} P_R D^i(R)_{ts} e^{-i*m*\alpha} \sum_n C_{n,m} e^{-i*m*\gamma} d^i(\beta)_{n,m} * Y_l^n(\theta,\varphi) \quad \text{(Eq. 17)}$$

These functions are tabulated by $|m| \leq l$ value for the point groups beginning on page 63 of Bradley and Cracknell. Some terms will have c or s next to them, symbolizing whether they do (s) or do not (c) have a multiple of $-i$ in the φ term. These multiplications symbolize whether the rotation represented is *improper*, i.e. has a flip in it. If it is improper, there is an s term. If both terms are present, then they are in a linear combination and must both be considered.

We will need scalar coefficients for the summed elements as well. These will come from the energy values of the electron and symmetry of the function in the crystal group. They are compiled in the tables starting at the bottom of page 71 of *Mathematical Theory of Symmetry in Solids* by l values mod a positive integer. Above the modulus, one adds all the elements of the group in that table as many times as they appear in the table. They then multiply this sum by n, where n is the smallest integer that reduces $l - n * modulus$ below the modulus.

Knowing the functions and coefficients, we can now construct the particular solution for our crystal type.

Expansion to Semiconductor Crystals

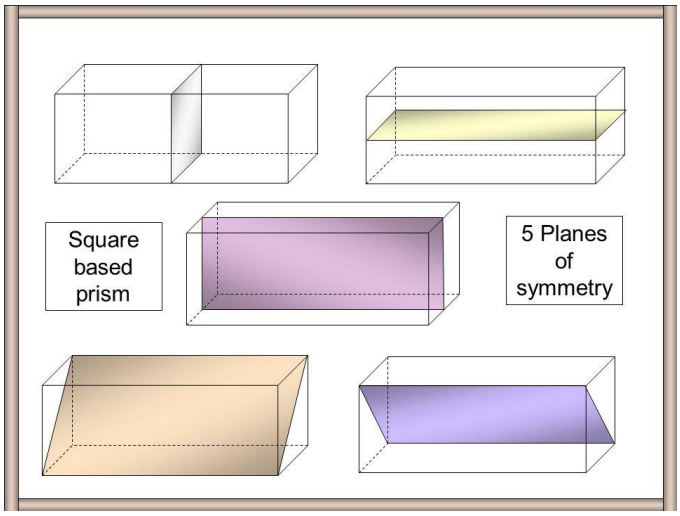
As previously acknowledged, the geometry of a crystal is assumed perfectly spatially symmetric. However, semiconductors, including optically active crystals, usually have impurities added, called *dopants*. These dopants either have excess or missing bonds, which can be approximated as particles referred to as *carriers*. Carriers are so approximated to allow them to move around the crystal and conduct electricity. However, we are more interested in the crystal's structural changes, so we have instead approximated them by the local deformations they cause, and allowed the deformations to travel as three-dimensional waves through an infinite crystal.

The particular crystal this section concerns is made from strontium barium niobate 60 ($Sr_6Ba_4Nb_{20}O_{60}$). It has been doped with cerium and rhodium (rare earth elements with many valence electrons) at a mass percentage of 1.6%. This makes it a relatively strong n-type semiconductor, because the majority of the charge carriers are electrons. This particular crystal undergoes the *photorefractive effect*, where photons from a laser source change the bond structure of the crystal by promoting valence electrons to act as carriers. This change in bond structure will locally affect the index of refraction, changing the way light bends (or *refracts*) in that part of the crystal.

There are some constraints on experimental setup to allow one to see the photorefractive effect. The source must be coherent, meaning the light's phase is nonrandom, and collimated, meaning the photon paths must be parallel, so that the light does not spread out over a long distance. Together, these two constraints mean one must use a laser. I used multiple helium neon lasers at 632.8nm for this purpose. In addition, the light must propagate along the optic axis of the crystal, which is the direction with the most activity; otherwise, the effect will be unnoticeable. The light also must align with the optic axis, so it must be *polarized* vertically. Polarization is a process where the electric field of light is constrained to only move in a certain direction. Finally, the magnetic field must rotate with the crystal structure, so one must make sure that the crystal is "upside up". Once placed in an experiment with these constraints, the photorefractive effect should be readily visible in a crystal with this type of activity.

From a crystallographic experiment, we know moderately doped strontium barium niobate ($SBN_{32\text{ to }82}$) belongs to the 4mm point group. This point group looks like a cube stretched along one axis. It has five plane symmetries, and one axial symmetry along the stretched axis where it can be rotated by $\frac{\pi}{2}$.

Figure 4, Plane Symmetries of the 4mm Point Group



We also know from this study that SBN_{60} belongs to the P4bm space group. The elements of this point group are, as 3x3 matrices:

$$\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix},\begin{bmatrix}-1&0&0\\0&-1&0\\0&0&1\end{bmatrix},\begin{bmatrix}0&-1&0\\1&0&0\\0&0&1\end{bmatrix},\begin{bmatrix}0&1&0\\-1&0&0\\0&0&1\end{bmatrix}$$

$$\begin{bmatrix}\frac{1}{2}-x&0&0\\0&\frac{1}{2}+y&0\\0&0&z\end{bmatrix},\begin{bmatrix}\frac{1}{2}+x&0&0\\0&\frac{1}{2}-y&0\\0&0&z\end{bmatrix},\begin{bmatrix}\frac{1}{2}+x&0&0\\0&\frac{1}{2}+y&0\\0&0&z\end{bmatrix},\begin{bmatrix}\frac{1}{2}-x&0&0\\0&\frac{1}{2}-y&0\\0&0&z\end{bmatrix}$$

These matrices can be understood to represent a group that is modeled as a hexagonal *P* lattice, which only has lattice points on the corners of the hexagon. It has *4* axes of rotation. The primary translation is by half a lattice length along the axis at $\frac{\pi}{4}$ to both x and y in the x-y plane, called the *b* axis. The presence of flips after translation adds the *m*.

We can then use these symmetries to find and construct the solution for a wave passing through an SBN_{60} crystal. The table found on page 65 of *Mathematical Symmetry of Solids* tells us that the m terms look as follows. Note that this book uses the Mulliken notation for point group elements. We can convert this back to the spherical harmonics knowing the l value.

Group Elements	**m mod +4**	**φ-dependence**
A_1	0	c
A_2	4	s
B_1	2	c
B_2	2	s
E	1	(c,s)
	3	(c,-s)

Next, we can use the table on page 72 to get the coefficients, or how many times the element appears in the summation. This is denoted in base four as

$$D^{4*n+\lambda} = n * reg + D^{\lambda} \text{ (Eq. 18)}$$

where n is a positive integer, and λ is the value of l less than four. The term reg contains a sum of each element of the group as many times as it appears. For instance, A_1 appears once in the above table, so it is in reg once. However, E appears twice, so it is in reg two times. The table of all the D^{λ} terms written out follows.

$\boldsymbol{l}$	**Term**
0	A_1
1	A_1+E
2	A_1+B_1+B_2+E
3	A_1+B_1+B_2+2E
reg	A_1+A_2+B_1+B_2+2E

These terms can then be used to write out our final sum of the wave function as

$$\sum_{\boldsymbol{l=4n}}\left(Y_l^{0\ mod\ 4}(\theta,\varphi) + n * reg\right) + \sum_{\boldsymbol{l=4n+1}}\left(Y_l^{0\ mod\ 4}(\theta,\varphi) + Y_l^{1\ mod\ 4}(\theta,\varphi) + n * reg\right) +$$
$$\sum_{\boldsymbol{l=4n+2}}\left(Y_l^{0\ mod\ 4}(\theta,\varphi) + Y_l^{2\ mod\ 4}(\theta,\varphi) + Y_l^{2\ mod\ 4}(\theta,-i*\varphi) + Y_l^{1\ mod\ 4}(\theta,\varphi) + n * reg\right) +$$
$$\sum_{\boldsymbol{l=4n+1}}\left(Y_l^{0\ mod\ 4}(\theta,\varphi) + Y_l^{2\ mod\ 4}(\theta,\varphi) + Y_l^{2\ mod\ 4}(\theta,-i*\varphi) + Y_l^{1\ mod\ 4}(\theta,\varphi) +\right.$$
$$\left. Y_l^{3\ mod\ 4}(\theta,i*\varphi) + n * reg\right) \text{ (Eq. 19)}$$

$$reg = Y_l^{0\ mod\ 4}(\theta,\varphi) + Y_l^{4\ mod\ 4}(\theta,-i*\varphi) + Y_l^{2\ mod\ 4}(\theta,\varphi) + Y_l^{2\ mod\ 4}(\theta,-i*\varphi) +$$
$$Y_l^{1\ mod\ 4}(\theta,\varphi) + Y_l^{3\ mod\ 4}(\theta,i*\varphi) \text{ (Eq. 20)}$$

Conclusion

We began this paper by stating what a crystal is, and worked our way through to finding the wave functions of an ideal SBN_{60} crystal. Now, it is time to explain why this model does not seem to predict the correct results in the crystal used in the physics experiment that motivated this thesis. The crystal structure examined does not reflect that in the experiment the crystal has multiple dopants. The dopants may change the symmetry in the crystal. We could modify this model to the crystal if we performed crystallographic studies to confirm its space and point groups. We would then repeat the procedure outlined for finding the symmetry-adapted functions of the crystal. However, previous attempts to so confirm the crystal shape have been met with equipment failure, so they must be done again.

Since this crystal is rather unique, it may be concluded that it is an outlier. Thus, some may suggest we focus more heavily on the single-doped crystals the model works on. However, the physics experiment was a preliminary material study, as double-doped crystals show promise in fixing some of the disadvantages of single-doped crystals. If we can conclude this crystal is somehow the standard for double-doped crystals, it would inform physicists and engineers greatly about the possible properties and disadvantages of optical semiconductors. Therefore, this crystal should not be ignored until we know more about it and others like it.

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