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# An Exploration of CRUM's and Algebraic CRUM Detection

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## 1. Background

- A crystal is a three-dimensionally periodic atomic solid. Its symmetries form a mathematical group, specially a crystallographic space group. There are only 230 crystallographic space group types. Every crystal possesses one of them.
- A space group possesses an infinite lattice of translational symmetries. Its translation factor group is finite, and is comprised of point symmetries, which each leave at least one point in the crystal invariant. Each element space-group consists of a lattice translation, and a combination of point operation and sub-lattice translation. A point operation that combines with a non-zero sub-lattice translation is referred to as “hybrid” (e.g. screw axis or glide plane).
- The unit cell is a region of the crystal with parallelepiped shape, which is repeated periodically at every point of the crystal lattice. The asymmetric unit is a wedge-shaped volume within the unit cell that contains all essential information about the crystal. Each element of the space-group copies the asymmetric unit to some other region of the unit cell or to one of its translational copies, until all space is filled. The number of asymmetric units within the unit cell is equal to the order of the point group.
- A crystal distortion is a change that lowers the symmetry of the crystal. We describe this change using an atomistic function and call it an *order parameter*. Examples include patterns of atomic displacements, magnetic moments, site occupancies, and polyhedral rotations.
- A phase transition gives rise to physical order parameters that lower the symmetry of a crystal. Though some symmetry elements of the parent structure are lost, some are retained in the child structure. These comprise the isotropy subgroup of the transition.
- Any symmetry-lowering distortion can be viewed as a linear superposition of order parameters, which could onset together or sequentially as temperature, pressure, or stoichiometry are varied. Order parameters could involve lattice strain, atomic displacements, molecular rotations, site occupancies, or magnetic moments.
- The symmetries of a crystal form a space group. A space group has matrix representations. The irreducible representations (we call them “irreps”) are recipes for symmetry breaking. An irrep order parameter is a crystal distortion that transforms using the irrep-matrix coefficients when a space group element is applied to it. An irrep order parameter of a crystal is a wave, and therefore has a specific  $\mathbf{k}$  vector in the first Brillouin zone of the reciprocal lattice. We call such a wave a *symmetry mode*.

- A rigid-unit is a collection of atoms within a crystal that move together in such a way as to preserve the internal structure (i.e. interatomic distances) of the collection. A rigid-unit mode (RUM) is a crystal distortion that rotates (or tilts) rigid units around fixed pivot points.
- In a 3D network of interconnected polyhedra (or molecules or some other rigid units), two neighboring rigid units are constrained to share one or two atoms (i.e. share a vertex or an edge). In such a network, a cooperative rigid-unit mode (CRUM) is a special type of RUM that occurs without breaking any of these share-atom constraints. The rigid-units all rotate about their own axes in a cooperative fashion so shared atoms remain shared.
- Like the asymmetric unit in real space, the Brillouin zone in reciprocal space has a fundamental wedge, so that every  $k$  point in reciprocal space is related by symmetry to a point in the fundamental wedge. We classify these points into a finite number of subspaces according to their location in the fundamental wedge, i.e. which symmetry-unique vertex, edge, or face they lie on. And the interior is all one region. The vertices are finite in number and are called special  $k$ -points – they tend to be high symmetry points. The other points (edges, faces, and interior) are non-special and infinite in number.
- Any crystal distortion can be expressed as a linear combination of order parameters of irreps of the space group of the crystal. This is a famous result from group representation theory (the orthogonality and completeness of irrep order parameters). This also applies to CRUM's.

The physical properties of many crystals (e.g. superconductors, zero-thermal-expansion compounds, ferroics and multiferroics, catalysts, etc) are sensitive to CRUM's. Cataloguing the CRUM's allowed by a given crystal can (1) help us to solve its structure experimentally, (2) allow us to understand its structure property relationships, and (3) improve our ability to strategically design and manipulate those properties for practical applications. Previous efforts have been made to identify CRUM's in several important materials classes. They employed strategies such as ball-and-spring simulations, phonon-frequency calculations, and trial-and-error searches. But none have been as simple or exhaustive as the algebraic approach developed by Prof. Branton Campbell's group at BYU during the past year.

## 2. Statement of Problems

2.1 Prof. Campbell's group has developed a new algebraic-search method for detecting CRUM's. The idea is to first parameterize all possible rigid-unit rotations with rotational symmetry modes, express each shared-atom displacement as a linear combination of symmetry-mode amplitudes (in the small-angle limit), set up a homogeneous system of equations of these relationships, and to solve that system. His group began by detecting CRUM's at special  $k$  points in cubic perovskites, which is a known result, and then proceeded to hexagonal and tetragonal tungsten bronzes (HTBs and TTBs respectively), where they were able to resolve some controversy. To further this investigation, I investigated perovskite CRUM's at non-special  $k$ -points, and compared my results to existing literature.

2.2 In exploring reciprocal space for CRUM's, either the M method or the MtM method could be employed. MtM was more sensitive to detecting CRUM's than M. The greater sensitivity of MtM allowed valid CRUM's that were slightly impure to be detected, which were not detected using M alone. However, the need for MtM arose because Mathematica's RowReduce routine was not sufficiently effective.

The fact that particular modes could be detected via MtM that were undetectable in M gave the impression that the two methods had different solution spaces. To investigate this idea further, the solution spaces of MtM and M were investigated by example and then theoretically, and turned out to be identical. At the same time, another student that I collaborated with developed a new row reduction routine. This new routine demonstrated concretely that we can use M alone to detect pure and slightly-impure CRUM's together. The key to the new routine was to evaluate a pivot for extinction using its absolute ratio to the largest residual value in the same column rather than by its absolute value alone.

2.3 Additionally, the rotational modes and displacive modes responsible for structural phase transitions in quartz and tridymite were explored using the ISODISTORT software suite, and the results were compared to existing literature.

### 3. Methodology

3.1 A CIF of lanthanum manganite ( $\text{LaMnO}_3$ ) was imported into the ISODISTORT software, where ISODISTORT's Method 2 was employed to apply a distortion at a specific non-special  $k$ -point, irrep, and order-parameter direction (OPD). The simplest OPD was selected for each point, although it does not matter which OPD is tested (if one works, they all work). The list of tested points is presented in Appendix 1. The selection of tested points was made with the following consideration: it is more revealing to test points with a varying denominator than with a varying numerator. This is because a CRUM is a wave with a specific wave vector; increasing the numerator from one simply multiplies  $k$  by an integer, which effectively generates harmonics similar to the fundamental wave vector.

The rotational symmetry modes of the child structure were saved in CIF format and used as the input for the Shared Shifts code written by Dr. Campbell and his research group. The output of this Shared Shifts code is a list of the modes that are CRUM's, and any linear dependencies that exist between modes for cooperative rotations to occur. The Shared Shifts code analyzed a unique CIF file for each non-special  $k$ -point that was tested.

3.2 To better understand how MtM was a more sensitive method than M, trigonometry was employed to create a symbolic matrix  $M$  that represented the atomic displacement due to an

infinitesimal distortion from an already distorted crystal. Taylor approximations were used to linearize the trigonometric functions. The effects of row reducing the resulting symbolic matrix, if made numerical, were considered.

Additionally, a symbolic upper triangular form matrix  $M$  was generated in Mathematica. The transpose of this matrix was taken and multiplied by itself. The pivot values of the resulting matrix and the results obtained from the symbolic trigonometric matrix provided enough information to reveal what made  $MtM$  a more sensitive CRUM detection method than  $M$  and why  $MtM$  had the tendency to ignore substantial mode impurities. The small pivot values in  $MtM$  tend to be the squares of the small pivot values of  $M$ , while the values above pivots tend to remain of the same magnitude. Thus impure (i.e. small) pivots in  $MtM$  are even more likely to be set to zero based on their smallness.

3.3 The beta CIF's of tridymite and quartz were produced in idealized versions, and the alpha CIF's of those two materials were produced using experimental data. Method 4 (mode decomposition) was employed via ISODISTORT to determine the distortions necessary to transform the beta structures to alpha structures.

## 4. Results

4.1 Every point tested on the T line in the reciprocal space of cubic perovskite using the  $T_4$  irreducible representation contains a CRUM. These are the only observed CRUM's that resulted from this investigation, and they confirm information presented in Swainson et. al (2009).

4.2  $MtM$  and  $M$  have the exact same solution spaces.  $MtM$  had an increased sensitivity in the CRUM detection process compared to  $M$  because  $MtM$  squared the pivots of the matrix. The terms that were responsible for generating false modes, as determined by trigonometric analysis, were sines and cosines of the small rotation angles. Thus, they could only obtain a maximum value of 1, and squaring them made them smaller. Depending on the tolerance, a sufficiently small term is truncated to zero in the row reduction process. However, if there is a small number that results purely from the error propagation of Mathematica's row reduction routine, truncating it to zero results in the invalid labeling of a non-CRUM as a CRUM.  $MtM$  has since been abandoned in favor of a more elegant, user-controlled row reduction routine that does not require as fine of a tolerance to detect CRUM's.

4.3 The CRUM's responsible for the structural phase transitions in tridymite are  $\Gamma_5^+$ ,  $\Gamma_5^-$ , and  $\Gamma_1^-$  with respect to beta-tridymite. The CRUM responsible for the structural phase transitions in quartz is  $\Gamma_3$  with respect to beta-quartz. These results agree with the results published by Pryde and Dove (1998). These CRUM's are especially interesting because they involve two pivot atoms with contrary rotations (parallel rotation pseudo-vectors). The shared atom is not torn

apart by these rotations because the pivot atoms are displaced in such a way that the effects of the rotation are negated—the shared atom remains fixed. While this is not a new discovery, it is an interesting and unusual case that generalizes what CRUM's can look like within our description.

## 5. Discussion

4.1 If ISODISTORT's capabilities are expanded to include the analysis of incommensurate modulations, then the exotic, incommensurate RUM surfaces that exist in cubic perovskites could be generated and verified using a similar methodology as the one described in 3.1. Other potential incommensurate surfaces could be investigated for a myriad of materials like HTB's and TTB's.

4.2 To gain greater control over the row reduction process, an original algorithm was prepared by Topper Yost, another member of Dr. Campbell's research group, based on our joint observations. Relative rather than absolute pivot values are evaluated against a user-specified tolerance. Partial rather than full pivoting is employed. Each step of the row reduction process can be displayed, so the user is completely aware of the role their selected tolerance plays in row reducing the matrix. This has been proven to be effective in determining CRUM's in TTB's and HTB's, and it eliminates the need for MtM—all modes can be detected via M.

4.3 Looking forward, ISODISTORT can be used to analyze the CRUM's responsible for the structural phase transitions in other silica polymorphs such as stishovite and coesite.

## 6. References

Swainson, I.P., Stock, C., Gehring, P.M. *et al.* (2009). *Phys. Rev. B*, **79**, 224301.  
Pryde, A.K.A. & Dove, M.T. (1998). *Phys. Chem. Minerals*, **26**, 171-179.

Appendix 1:  
Non-Special  $k$ -point Investigation in Cubic Perovskite

Non-Special $k$ -line	Irrep	a =	b =	c =	Non-Special $k$ -space	Irrep	a =	b =	c =
$\Lambda$ (a,a,a)	$\Lambda_2$	1/3			$C$ (a,a,c)	$C_1$	1/3		1/4
	$\Lambda_2$	1/4				$C_1$	1/4		1/3
	$\Lambda_2$	1/5				$C_1$	1/3		1/5
	$\Lambda_2$	1/8				$C_1$	1/5		1/3
	$\Lambda_3$	1/3				$C_1$	1/4		1/5
	$\Lambda_3$	1/4				$C_1$	1/5		1/4
	$\Lambda_3$	1/5				$C_2$	1/3		1/4
	$\Lambda_3$	2/5				$C_2$	1/4		1/3
	$\Lambda_3$	1/6				$C_2$	1/3		1/5
	$\Lambda_3$	1/7				$C_2$	1/5		1/3
	$\Lambda_3$	1/8				$C_2$	1/4		1/5
	$\Lambda_3$	3/8				$C_2$	1/5		1/4
	$\Lambda_3$	1/10			$A$ (a,b,0)	$A_1$	1/3	1/4	
	$\Lambda_3$	3/10				$A_1$	1/4	1/3	
	$\Lambda_3$	1/11				$A_1$	1/3	1/5	
	$\Lambda_3$	1/12				$A_1$	1/5	1/3	
	$\Lambda_3$	5/12				$A_1$	1/4	1/5	
$\Delta$ (0,b,0)	$\Delta_4$		1/3			$A_1$	1/5	1/4	
	$\Delta_4$		1/4			$A_2$	1/3	1/4	
	$\Delta_4$		1/5			$A_2$	1/4	1/3	
	$\Delta_5$		1/3			$A_2$	1/3	1/5	
	$\Delta_5$		1/4			$A_2$	1/5	1/3	
	$\Delta_5$		1/5			$A_2$	1/4	1/5	
$\Sigma$ (a,a,0)	$\Sigma_2$	1/3				$A_2$	1/5	1/4	
	$\Sigma_2$	1/4			$B$ (a,1/2,c)	$B_1$	1/3		1/4
	$\Sigma_2$	1/5				$B_1$	1/4		1/3
	$\Sigma_3$	1/3				$B_1$	1/3		1/5
	$\Sigma_3$	1/4				$B_1$	1/5		1/3
	$\Sigma_3$	1/5				$B_1$	1/4		1/5
	$\Sigma_4$	1/3				$B_1$	1/5		1/4
	$\Sigma_4$	1/4				$B_2$	1/3		1/4
	$\Sigma_4$	1/5				$B_2$	1/4		1/3
$S$ (a,1/2,a)	$S_2$	1/3				$B_2$	1/3		1/5
	$S_2$	1/4				$B_2$	1/5		1/3
	$S_2$	1/5				$B_2$	1/4		1/5
	$S_3$	1/3				$B_2$	1/5		1/4

	<b>S<sub>3</sub></b>	1/4			<b>GP (a,b,c)</b>	<b>GP<sub>1</sub></b>	1/3	1/4	1/5
	<b>S<sub>3</sub></b>	1/5				<b>GP<sub>1</sub></b>	1/4	1/3	1/5
	<b>S<sub>4</sub></b>	1/3				<b>GP<sub>1</sub></b>	1/3	1/5	1/4
	<b>S<sub>4</sub></b>	1/4				<b>GP<sub>1</sub></b>	1/4	1/5	1/3
	<b>S<sub>4</sub></b>	1/5				<b>GP<sub>1</sub></b>	1/5	1/4	1/3
<b>T (1/2,1/2,c)</b>	<b>T<sub>4</sub></b>			1/3		<b>GP<sub>1</sub></b>	1/5	1/3	1/4
	<b>T<sub>4</sub></b>			1/4					
	<b>T<sub>4</sub></b>			1/5					
	<b>T<sub>4</sub></b>			2/5					
	<b>T<sub>4</sub></b>			1/6					
	<b>T<sub>4</sub></b>			1/7					
	<b>T<sub>4</sub></b>			1/8					
	<b>T<sub>4</sub></b>			1/9					
	<b>T<sub>4</sub></b>			1/10					
	<b>T<sub>4</sub></b>			1/12					
	<b>T<sub>5</sub></b>			1/3					
	<b>T<sub>5</sub></b>			1/4					
	<b>T<sub>5</sub></b>			1/5					
	<b>T<sub>5</sub></b>			2/5					
	<b>T<sub>5</sub></b>			1/6					
	<b>T<sub>5</sub></b>			1/7					
	<b>T<sub>5</sub></b>			1/8					
	<b>T<sub>5</sub></b>			1/10					
	<b>T<sub>5</sub></b>			1/12					
<b>Z (a,1/2,0)</b>	<b>Z<sub>2</sub></b>	1/3							
	<b>Z<sub>2</sub></b>	1/4							
	<b>Z<sub>2</sub></b>	1/5							
	<b>Z<sub>3</sub></b>	1/3							
	<b>Z<sub>3</sub></b>	1/4							
	<b>Z<sub>3</sub></b>	1/5							
	<b>Z<sub>4</sub></b>	1/3							
	<b>Z<sub>4</sub></b>	1/4							
	<b>Z<sub>4</sub></b>	1/5							