SYMMETRY CHANGES IN RANK-LOWERING PHASE TRANSITIONS

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ABSTRACT

We describe, using the example of the one non–trivial rank–4 orthorhombic Bravais class, a procedure to determine the low-rank space groups that can arise from a given high-rank space group through a continuous phase transition.

Consider a continuous structural phase transition whose only effect in Fourier space is a slight distortion of the lattice of wave vectors that lowers its rank, possibly with a reduction of its point group. Suppose we know the space group describing the crystal in its high-rank phase. What are the possible space groups describing the crystal in its low-rank phase? We illustrate here how this question is answered in the language of Fourier space crystallography.*

When the rank is lowered, two issues arise that are not relevant to rank-preserving transitions. (1) Lowering the rank introduces new linear relations among formerly independent wave vectors. This imposes new constraints on the linear phase functions that describe the point group symmetry of the material. If a phase function fails to satisfy these constraints the associated point group element is lost and the symmetry of the material is reduced. (2) Lowering the rank reduces the gauge freedom existing in the high-rank phase, making it possible to distinguish low-rank structures that are indistinguishable in the high-rank phase. As a result a single high-rank space group may give rise to more than one low-rank space group.

We illustrate this with the rank-4 orthorhombic space groups with point group mmm in the O Bravais class.† Lattices in this class contain wave vectors of the form

$$\mathbf{k} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c}_1 + m\mathbf{c}_2, \quad h+l \text{ and } k+m \text{ even}, \tag{1}$$

where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}_1$ are mutually orthogonal wave vectors and $\mathbf{c}_1 = \gamma\mathbf{c}_2$ with γ irrational. We examine the continuous phase transition in which γ becomes the ratio of two relatively prime integers, n_1/n_2.

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* The relevant terms and concepts of Fourier-space crystallography are summarized in the Appendix.

† This is one of the two non-trivial rank-4 Bravais classes enumerated in Ref. 1. It also appears in a separate paper in this volume on the description of composite crystals.

$rank-4\ O-lattice$				$rank-3\ F^*-lattice$				
$\mathbf{b}_1$=$\mathbf{a}$+$\mathbf{c}_1$, $\mathbf{b}_2$=$\mathbf{a}$−$\mathbf{c}_1$, $\mathbf{b}_3$=$\mathbf{b}$+$\mathbf{c}_2$, $\mathbf{b}_4$=$\mathbf{b}$−$\mathbf{c}_2$.				$\mathbf{B}_1$=$\mathbf{b}$+$\mathbf{c}$, $\mathbf{B}_2$=$\mathbf{c}$+$\mathbf{a}$, $\mathbf{B}_3$=$\mathbf{a}$+$\mathbf{b}$.				
mmm S.G.	Φ_{m_a}	Φ_{m_b}	Φ_{m_c}	mmm S.G.	Φ_{m_a}	Φ_{m_b}	Φ_{m_c}	$mm2$ S.G.
(i)	0000	0000	0000	(71)	000	000	000	(44)
(ii)	$00\frac{1}{2}\frac{1}{2}$	0000	0000	(74)	$\frac{1}{2}\frac{1}{2}0$	000	000	(46)
(iii)	$00\frac{1}{2}\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}00$	0000	(72)	$\frac{1}{2}\frac{1}{2}0$	$0\frac{1}{2}\frac{1}{2}$	000	(45)
				(73)	$\frac{1}{2}\frac{1}{2}0$	$0\frac{1}{2}\frac{1}{2}$	$\frac{1}{2}0\frac{1}{2}$	–
$(\mathbf{b}_1\ \mathbf{b}_2\ \mathbf{b}_3\ \mathbf{b}_4) = (\mathbf{B}_1\ \mathbf{B}_2\ \mathbf{B}_3) \begin{pmatrix} \ell & -(\ell+1) & (j+1) & -j \\ (\ell+1) & -\ell & j & -(j+1) \\ -\ell & (\ell+1) & -j & (j+1) \end{pmatrix}$								

Table1. Primitive generating vectors for the rank-4 O-lattice and rank-3 F^*-lattice are given at the top in terms of the vectors in Eqs. (1) and (2). Their linear relations when γ=n_1/n_2=$(2\ell+1)/(2j+1)$ are given at the bottom. In between are listed the space groups with point group mmm and $mm2$ in the form $\Phi_g(\mathbf{b}_i)\equiv\theta_1\theta_2\theta_3\theta_4$ on the O-lattice and in the form $\Phi_g(\mathbf{B}_j)\equiv\theta_1\theta_2\theta_3$ on the F^*-lattice, taken from Refs. 3 and 4. For the $mm2$ space groups disregard the phase function associated with m_c. The rank-3 space group numbers follow the International Tables.

Step 1 – Find the possible low-rank Bravais classes.

Let $\mathbf{c}_1 = n_1\mathbf{c}$ and $\mathbf{c}_2 = n_2\mathbf{c}$ so that (1) becomes

$$\mathbf{k} = h\mathbf{a} + k\mathbf{b} + (n_1 l + n_2 m)\mathbf{c}, \quad h+l \text{ and } k+m \text{ even.} \tag{2}$$

Depending on the parities of n_1 and n_2 the possible Bravais classes of the rank-3 reciprocal lattice are: *(1) base-centered orthorhombic*, in an A setting when n_1 is even and n_2 is odd, and in a B setting when n_1 is odd and n_2 is even; *(2) face-centered orthorhombic*, F^* (body centered in real space), when n_1 and n_2 are both odd. We illustrate the next steps in the case where the low-rank lattice is F^*, taking $n_1 = 2\ell + 1$ and $n_2 = 2j + 1$.

Step 2 – Express the vectors in the low-rank lattice that correspond to the high-rank primitive lattice generating vectors in terms of primitive generating vectors of the low-rank lattice.

These relations are of the form

$$\mathbf{b}_i = \sum_{j=1}^{d} \mathbf{B}_j m_{ji}\ , \qquad i = 1 \ldots D > d. \tag{3}$$

Their explicit form in the case of the O to F^* transition is given in in Table 1.

Step 3 – Resolve the high-rank gauge-equivalence class into low-rank gauge-equivalence classes.

A general high-rank gauge transformation on a set of phases specifying the high-rank space group parametrizes the entire high-rank gauge-equivalence class by D numbers – the values $\chi(\mathbf{b}_i)$ of the linear gauge function on the primitive generators of the high-rank lattice. We can single out a unique representative of each low-rank gauge-equivalence class by choosing a particular low-rank gauge that fixes d of these D independent parameters. This insures that the sets of low-rank phase functions specified by the remaining $D-d$ parameters will not be gauge-equivalent and therefore will describe distinguishable structures. The low-rank phase functions arrived at in this way will be given in a particular gauge. They can be identified with the sets of tabulated phases used to specify the low-rank space groups by comparing gauge invariant linear combinations.

In our example we can make a low-rank gauge transformation (determined by inverting the first three columns of the m_{ji} matrix in Table 1) that sets $\chi(\mathbf{b}_i)$ to 0, $i = 1, 2, 3$, leaving only a single parameter $\chi_0 \equiv \chi(\mathbf{b}_4)$.

With this choice of low-rank gauge the general form for each rank-4 phase function given in Table 1 reduces to:

$$\Phi_{m_a}(\mathbf{b}_i) \equiv 0\,0\,\theta_1\theta_1; \quad \Phi_{m_b}(\mathbf{b}_i) \equiv \theta_2\theta_2\,(-\chi_0)(-\chi_0); \quad \Phi_{m_c}(\mathbf{b}_i) \equiv 0\,0\,\chi_0(-\chi_0); \quad (4)$$

where θ_1 and θ_2 are gauge-invariant phases equal to 0 or $\frac{1}{2}$ given by identifying (4) with the entries in the Table when $\chi_0 = 0$. By using this more general form we obtain *all* the possible rank-3 space groups.

Step 4 – Find phases describing low-rank space groups that agree with the phases for the high-rank space group as expressed in the general form of Step 3.

We look for the largest subgroup of the high-rank point group contained in the point group of the low-rank lattice, whose elements g can be assigned phases $\Phi_g(\mathbf{B}_j)$ at the generators of the low-rank lattice agreeing with one of the forms of the high-rank phases:

$$\Phi_g(\mathbf{b}_i) \equiv \sum_{j=1}^{d} \Phi_g(\mathbf{B}_j) m_{ji} \ . \quad (5)$$

The phases $\Phi_g(\mathbf{B}_j)$ must differ at most by a low-rank gauge transformation from a set describing a known space group. Such a subgroup can be a point group for the low-rank structure and the phases $\Phi_g(\mathbf{B}_j)$ specify the corresponding low-rank space group.

Table 1 lists the phases associated with the F^*-lattice that specify the space groups associated with point groups mmm and $mm2$. With the left side of (5) taken to be each of the 12 high rank phases in (4) we seek to satisfy (5) with low-rank phases from Table 1, or with phases that are low-rank gauge-equivalent to the ones in Table 1. The problem of choosing the correct low-rank gauge is solved by noting that there are 6 gauge-invariant linear combinations of low-rank phases:‡ $\Phi_{m_a}(\mathbf{B}_1)$,

‡ They are gauge invariant because $\mathbf{B}_1$ and $\mathbf{B}_2 - \mathbf{B}_3$ lie in the invariant plane of m_a.

rank-4 S.G. :	(i)	(ii)	(iii)
χ_0=0 mod $\frac{1}{n_1}$	(71) $Immm$	(74) $Ibmm$	(72) $Ibam$
$\chi_0=\frac{1}{2n_1}$ mod $\frac{1}{n_1}$	(74) $Imma$	(72) $Ibma$	(73) $Ibaa$
χ_0 arbitrary	(44) $Imm2$	(46) $Ibm2$	(45) $Iba2$

Table2. The rank-3 space groups that can arise from each of the rank-4 orthorhombic space groups on the O-Bravais class specified in Table 1, when $\mathbf{c}_1=(n_1/n_2)\mathbf{c}_2$ with n_1 and n_2 both odd integers. The space groups with n_1+n_2 odd are given by replacing the I symbol by an A if n_1 is even and then transforming into a B setting if n_2 is even.

$\Phi_{m_a}(\mathbf{B}_2-\mathbf{B}_3)$ and the two other pairs derived from these by cyclic permutations of a,b,c and $1,2,3$. (Table 1 shows that the members of each pair are either both 0 or both 1/2, so the six gauge invariant phases are entirely specified by three independent numbers.) These leave three linearly independent phases ($\Phi_{m_a}(\mathbf{B}_2)$ and its cyclic permutations) which can be assigned arbitrary values by the three degrees of low-rank gauge freedom.

When we remove from the 12 equations (5) those that merely specify the values of the gauge dependent phases and those that are not linearly independent of the others, we arrive at the four relations to the left of the arrow in (6). The first two contain gauge-invariant phases and there is a single gauge-invariant linear combination of the last two, resulting in the three conditions to the right of the arrow.

$$\left\{\begin{array}{l}\Phi_{m_a}(\mathbf{b}_3)\equiv\ \theta_1\ \equiv (2j{+}1)\Phi_{m_a}(\mathbf{B}_1)\\ \Phi_{m_b}(\mathbf{b}_1)\equiv\ \theta_2\ \equiv (2\ell{+}1)\Phi_{m_b}(\mathbf{B}_2)\\ \Phi_{m_c}(\mathbf{b}_1)\equiv\ 0\ \equiv (2\ell{+}1)\Phi_{m_c}(\mathbf{B}_2)\\ \Phi_{m_c}(\mathbf{b}_3)\equiv\ \chi_0\ \equiv (2j{+}1)\Phi_{m_c}(\mathbf{B}_1)\end{array}\right. \quad\Longrightarrow\quad \left\{\begin{array}{l}\Phi_{m_a}(\mathbf{B}_1)\equiv\ \Phi_{m_a}(\mathbf{b}_3)\\ \Phi_{m_b}(\mathbf{B}_2)\equiv\ \Phi_{m_b}(\mathbf{b}_1)\\ \Phi_{m_c}(\mathbf{B}_1{-}\mathbf{B}_2)\equiv\ n_1\chi_0\end{array}\right. . \qquad (6)$$

The three independent gauge-invariant low-rank phases appearing on the right side of (6) uniquely determine the low-rank space group. When $n_1\chi_0\not\equiv 0,\frac{1}{2}$ the m_c mirror is removed from the low-rank point group and the new point group is $mm2$. The resulting space groups are summarized in Table 2. A similar application of the procedure yields the rank-3 space groups in the cases where n_1+n_2 is odd. They are obtained from Table 2 by replacing the symbol I by A if n_1 is even and then transforming to a B setting if n_2 is even.

Appendix — Fourier-Space Crystallography[3]

A *crystal* is any solid having a discrete diffraction diagram. The (reciprocal) *lattice* L (the Fourier module) is the set of all integral linear combinations of wave vectors in the diffraction diagram. Its *rank* D is the smallest number of wave vectors needed to generate it. Two lattices of wave-vectors are in the same Bravais class if one can interpolate between them with a sequence of lattices, all with the same point group and rank.

Two densities ρ and ρ' are *indistinguishable* if they have the same distribution of substructures on any scale, or equivalently,* if their density Fourier coefficients are related by

$$\rho'(\mathbf{k}) = e^{2\pi i\chi(\mathbf{k})}\rho(\mathbf{k}) \ , \tag{A.1}$$

where χ, called a *gauge function* is linear modulo an integer over the lattice of wave vectors. The function χ is completely specified by its independent values on a set of D wave vectors which primitively generate the lattice.

The *point group G of a crystal* is the set of all operations from $O(3)$ that leave the density indistinguishable. Associated with every point group element g is a gauge function $\Phi_g(\mathbf{k})$ (a *phase function*), giving the relation between density Fourier coefficients at symmetry related points:

$$\rho(g\mathbf{k}) = e^{2\pi i\Phi_g(\mathbf{k})}\rho(\mathbf{k}) \ . \tag{A.2}$$

The symmetry class of a crystal is specified by its point group along with a set of phase functions.

Two indistinguishable densities must have the same space group. Their phase functions are related by a *gauge transformation*:

$$\Phi'_g(\mathbf{k}) \equiv \Phi_g(\mathbf{k}) + \chi([g-1]\mathbf{k}) \ , \tag{A.3}$$

and are called *gauge-equivalent*. The *space group* of a crystal is specified by a class of gauge-equivalent phase functions.

Phase functions must satisfy the *group compatibility condition*:

$$\forall g,h \in G: \qquad \Phi_{gh}(\mathbf{k}) \equiv \Phi_g(h\mathbf{k}) + \Phi_h(\mathbf{k}), \tag{A.4}$$

which enables one to specify the space group by giving only the values of the phase functions associated with the generators of the point group at a set of lattice–generating vectors.

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4. References

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* For a proof of this see page 7 of Ref. 3.