

Structural Phase Transitions

Exercises on applications of group theory – part B

(using internet tools from the Bilbao Crystallographic Server and ISOTROPY)

B1. A structure has symmetry $Pnma$. At lower temperatures, a phase transition happens, and diffraction experiments show that superstructure reflections at points $(h, k, l + 1/2)$ appear indicating the duplication of the c parameter, while keeping an orthorhombic lattice. Assuming a group-subgroup related transition and using CELLSUB, predict the only two possible space groups of this low-temperature phase, and the transformation matrix relating them with the parent space group $Pnma$. Using COPL from the ISOTROPY package or SYMMODES of the Bilbao Crystallographic Server check that these two space groups are isotropy subgroups of $Pnma$. Identify in each case the wave vector and label of the active irrep of the transition. Check by hand that indeed these irreps yield the superlattice that has been observed.

B2. Using SYMMODES, do again exercise A3, and obtain the graph of all intermediate subgroups between the space groups of high and low temperature.

B3. Repeat exercise A4 using SYMMODES and INVARIANTS

B4. A structure is pseudosymmetric with respect to a structure with $Pmmm$ space group, and its symmetry is described by $P11m$, with the same unit cell.

i) Obtain the graph of maximal subgroups relating both symmetries.

ii) With SYMMODES, identify the possible irrep distortions present in the monoclinic structure and their isotropy subgroups. Detect that the $P11m$ structure cannot be reached with a single order parameter, and two active irrep are necessary.

iii) Obtain the possible frozen modes for an atom occupying a site $2i$. Checking the form of the type of mode for each irrep (or its isotropy subgroup), obtain the equivalence of the labels used in SYMMODES with those used in exercise 3 of the tutorial.

(*Symmodes only works with conventional settings for the description of the subgroup*)

B5. A structure of symmetry $P4/mmm$ suffers a transition into a distorted monoclinic phase with space group $P2/m11$ ($\mathbf{a}, \mathbf{b}, \mathbf{c}; 000$), i.e. the monoclinic axes is along the x direction and the lattice does not change.

i) using SYMMODES obtain the graph of maximal subgroups relating the two symmetries

ii) Identify the active irrep.

iii) Check that for an atom $4j$ the primary mode will only involve displacements along the z direction, while secondary displacements (expected to be weaker) will happen on the plane xy

iii) Use the program INVARIANTS from ISOTROPY available in internet to obtain the other possible symmetries, which could be produced by the same order parameter.

B6. Show that the two symmetry breaks $Pmmm \rightarrow Pmmb (a,4b,c)$ and $Pmmm \rightarrow Pmm2 (a,3b,c)$ (with origin shift in the transformation unknown) can be produced by the same irrep of the little co-group, by changing only the modulus of the wave vector k on the line Δ of the Brillouin zone.

B7. Distorted perovskites

$CeAlO_3$ is a perovskite ABX_3 with three distorted phases in different temperature ranges, of symmetries $I/4mcm (Z=4)$, $Imma (Z=4)$ and $R-3c (Z=6)$. The structure has the ideal perovskite structure only at high temperatures: cubic $Pm-3m (Z=1)$ with positions: A 1b, B 1a, X 3d.

i) Derive that the three distorted phases are probably caused by a single 3-dim active irrep, i.e. the same 3-dim order parameter causes the three phases by taking different directions within its 3-dim space. (*Hint: use SYMMODES starting with the trigonal structure and then with the orthorhombic one, to derive possible active irreps, and show that the scenario of a single active irrep is possible*).

ii) Assuming that a single irrep distortion is indeed responsible of the three phases, obtain the possible transformation matrices, including origin shift, relating each of the three space groups with the cubic one.

iii) Using TRANSTRU obtain the asymmetric unit for each phase. In each case, indicate which atomic coordinate or coordinates are to be refined