Hands-on exercises on the use of some tools of the Bilbao Crystallographic Server for the analysis of Structural Phase Transitions.

1. Limiting the possible symmetries of a distorted phase (*example 2 in Tutorial of SUBGROUPS*)

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.

(i). Assuming a group-subgroup related transition and using SUBGROUPS, predict the only two possible space groups of this low-temperature phase, and the transformation matrix relating it with the parent space group Pnma.

(ii). What is the wave vector associated with the order parameter of this transition?

(iii) Using the Get_irreps link within SUBGROUPS determine if the space groups determined in (i) are isotropy subgroups of an irrep, and in each case, identify the label of the active primary irrep of the transition.

(iv) From the output of Get_irreps, in both cases identify the irrep associated with a secondary polar distortion mode.

(v) Determine using SUBGROUPS all the possibles symmetries that could happen in a phase transition with this wave vector, under the constraint that the Landau assumption is fulfilled (the order parameter transforms according to a single irrep).

2. Monoclinic phase of the system $PbZr_{1-x}Ti_xO_3$ (PZT)

Consider the perovskite-like ferroelectric system $PbZr_{1-x}Ti_xO_3$ (PZT). Measurements have revealed a monoclinic phase (with no cell multiplication) between the previously established tetragonal (*P4mm*) and rhombohedral (*R3m*) regions in its phase diagram as a function of x. Both phases, *P4mm* and *R3m*, are ferroelectric distorted phases of the perovskite, due to the condensation of a polar mode at k=0. The perfect perovskite structure $PbBO_3$ is cubic *Pm_3m* (Z=1) with positions: Pb 1b, B 1a, O 3d.

(i) Using SUBGROUPS/Get_irreps obtain a valid transtormation matrix for the pairs *Pm_3m*->*P4mm*, and *Pm_3m* -> *R3m*, and check that indeed the two phases, *P4mm* and *R3m*, can be assigned to the same active irrep, for two different directions of the order parameter. Take notice of the active irrep and these directions.

(ii) A reasonable assumption about the detected monoclinic structure is that it must be some bridging phase with the order parameter changing between the two special directions obtained in (a). Its symmetry would then be given by a common subgroup of the tetragonal and rhombohedral space groups, corresponding to the same order parameter, i.e. the same irrep, but for a more general direction. Use SUBGROUPS to predict under this assumption the space group of this monoclinic phase.

(iii) Use TRANSTRU to derive a starting structural model of the monoclinic phase (with a single mixed site for the Zr/Ti atoms), which you could use as the starting point for a refinement of the structure.

3. $BiFeO_3$: A phase with two order parameters

The multiferroic $BiFeO_3$ has symmetry *R3c* with Z=6 at room-temperature, and is a

distorted perovskite, with a virtual parent cubic *Pm-3m* structure (Fe: 1a, Bi: 1b, O: 3d, $a_c \approx 3.97$ Å).

(i) Using SYMMODES, show that the room temperature phase of $BiFeO_3$ has two active irreps.

(ii) Some publications have reported an intermediate phase with symmetry *I4/mcm*. Using SUBGROUPS crosscheck the plausibility of this intermediate symmetry as originating from the same order parameters (one or both) which are active in the *R3c* phase.

(iii) With TRANSTRU produce a starting structural model to refine the structures *I4/mcm* and *R3c* of $BiFeO_3$, indicating the refinable coordinates of the constructed asymmetric unit.