Structural Phase Transitions
Exercises on applications of group theory – part A

A1. A hexagonal structure suffers a phase transition and superstructure reflections of type (1/2,1/2,0) are detected. Determine all the possible lattices that may correspond to this structure, by giving for each of them the corresponding supercell.
(*Hint: the detection of superstructure reflections allows to identify the irrep star of* ***k*** *vectors, and the sublattice of the distorted phase will be given by the set of lattice translations* ***T*** *that fullfill* $exp[i2\pi \mathbf{k}.\mathbf{T}]=1$ *for all or a subset of* ***k****-vectors of the star*)

A2. A compound suffers a phase transition with the symmetry change *I4/mmm* ---- *Fmmm* with the settings related by the tranformation **a-b**, **a+b**, **c**; 0 0 0. Derive which ferroic properties will be present in the distorted structure, the number of domains. Identify the active irrep of the transition and a possible order parameter. (*to shorten the exercise, consider that the active irrep is one-dimensional*)

A3. A compound has *Pnma* symmetry at high temperatures and has space group $P12_11$ at low temperatures, keeping essentially the same lattice, except for some strain. Show that at least two irreps must be active to explain the symmetry of the distorted structure. Identify the possible active irreps in the distorted phase. Predict the possible (alternative) symmetries of a probable intermediate phase. (*If two different irreps are primary in the symmetry break, it is probable that they will act separately producing two subsequent transitions*)

A4. A structure of symmetry *P4/mmm* suffers a transition into a distorted monoclinic phase with space group *P2/m11* (**a**,**b**,**c**; 000), i.e. the monoclinic axes is along the x direction and the lattice does not change.
i) How many distinct types of domains one should expect? ii) Show that this phase could be due to some primary distortion with symmetry given by the irrep E_g (see attached Table), and no other irrep could explain this symmetry break. ii) If subsequently the system suffers another transition into a phase with different symmetry, and one considers it is due to the same active irrep, predict the symmetry of this second phase.
iii) See the attached graph of minimal subgroup relating the two groups. Show that the irrep B_{1g} has the intermediate subgroup *Pmmm* as isotropy subgroup. Distortions of this symmetry will therefore appear as a secondary effect.
iv) Show that indeed the product Eg x Eg x B1g contains the identity irrep. What type of lowest coupling will happen then between the order

parameter of symmetry E_g and the secondary modes B_{1g}? (*Hint: the possible isotropy subgroups of the one-dimensional irreps can be obtained by inspection of the Table. For the bidimensional ones show that E_u does not subduce the identity irrep in the subgroup P2/m11, while Eg does. For this last case, deduce the isotropy subgroups for the special directions (1,0), (0,1), (1,1) and (1,-1)*)

A5. A compound with parent symmetry Pmmm exhibits a series of phase transitions into superstructures with the parameters b multiplied by 6, 4, 7 and 3. They are due in principle to a distortion varying its wave vector along **b***, but keeping the same rotational symmetry given by the same small irrep. In these phases the strongest superstructure reflections happen for wave vectors **q**= β**b*** with beta=1/6, 1/4, 2/7 and 1/3, respectively. The space group of the phase with b-parameter = 4b has been identified as Pbmm keeping the same setting (or Pmma in conventional setting). Predict the possible symmetries of the other phases. Show that the phases with cell multiplication 3 and 7 (and only these phases) can be ferroelectric phases, and their polar axis will be along the x axis.
(*One should construct the bidimensional matrices of the active irrep and derive the isotropy subgroups as a function of the parity of the wave vector. The active irrep can be identified from the knowledge of the isotropy subgroup observed for a given wave vector*)

A6. Consider a structure *Pmmm* with an atom located at position 2i (x 0 0). We enumerate its orbit in the following form: atom 1 : (x,0,0) ; atom 2: (-x,0,0). A distorted phase of this structure is the result of the consecutive condensation of two soft-modes. In one of them, the atoms above have strong displacements along the z axis according to the following pattern (repeated in all unit cells): (1 0 0; 1 0 0) (we list the three components of the displacements of the two atoms indicated above).
i) Show that this soft-mode has a symmetry given by the irrep B_{3u} of Pmmm at the Brillouin zone centre. Derive the space group of the structure if only a distortion of this symmetry is present. Show that the structure will be polar (ferroelectric) with a spontaneous polarization along the x axis.

The second soft-mode involves considerable displacements of the same atoms along the y direction with the pattern: (0 1 0; 0 -1 0).
ii) Show that this second frozen mode has symmetry B_{1g}. Deduce the space group of the structure with these two soft-modes frozen.
iii) Show that B_{3u} x B_{1g} x B_{2u} = identity irrep, and therefore invariants of type Q_{B3u} Q_{B1g} Q_{B2u}, trilinear in the amplitudes of the two soft-mode and any additional mode of symmetry B2u, are possible.
iv) Using the result of iii) construct an elementary Landau potential for this phase, and by minimizing it show that modes of symmetry B_{2u} will be

spontaneous in the phase, as secondary induced frozen modes, with an amplitude proportional to the product of the two primary soft-modes.
v) Show that a distortion mode of type (0 1 0; 0 1 0) for the atoms at 2i has the symmetry B_{2u} of the allowed secondary modes, and therefore will also be frozen in the structure, although with smaller amplitude than the primary soft-modes.

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exercise out of program:

A0. The thiourea has a parent structure of Pnma symmetry, and exhibits an incommensurate phase due to a displacive modulation with symmetry given by the small irrep τ_4 (see attached Table) for a wave vector of type β**b***. Its phase diagram has also a commensurate phase due to the lock-in of the wave vector into a commensurate value with $\beta=1/9$.
i) Show that in this phase the unit cell will be multiplied by 9, and in general the symmetry operations $(2_y|0\ 9/2\ 0)$, $(m_x|1/2\ 9/2\ 1/2)$ and $(m_z|1/2\ 0\ 1/2)$ will be maintaned.
ii) Show also that if the amplitude of the modulation is real (the phase of the complex amplitude is cero) the inversion operation $(i|0\ 0\ 0)$ will also be conserved. Predict then the space group of this phase under this situation.
(*This exercise requires to know how to contruct an elementary bidimensional irrep of a space group from a small irrep for k≠0. Using programs of the BCS or Isotropy can shorten the task to a minimum*)

Table 1: Irreps of the point group 4/mmm

Character Table												
D_{4h}(4/mmm)	#	1	2	4	2_h	$2_{h'}$	-1	m_z	-4	m_v	m_d	functions
Mult.	-	1	1	2	2	2	1	1	2	2	2	_
A_{1g}	Γ_1^+	1	1	1	1	1	1	1	1	1	1	x^2+y^2,z^2
A_{2g}	Γ_2^+	1	1	1	-1	-1	1	1	1	-1	-1	J_z
B_{1g}	Γ_3^+	1	1	-1	1	-1	1	1	-1	1	-1	x^2-y^2
B_{2g}	Γ_4^+	1	1	-1	-1	1	1	1	-1	-1	1	xy
E_g	Γ_5^+	2	-2	0	0	0	2	-2	0	0	0	(xz,yz),(J_x,J_y)
A_{1u}	Γ_1^-	1	1	1	1	1	-1	-1	-1	-1	-1	_
A_{2u}	Γ_2^-	1	1	1	-1	-1	-1	-1	-1	1	1	z
B_{1u}	Γ_3^-	1	1	-1	1	-1	-1	-1	1	-1	1	_
B_{2u}	Γ_4^-	1	1	-1	-1	1	-1	-1	1	1	-1	_
E_u	Γ_5^-	2	-2	0	0	0	-2	2	0	0	0	(x,y)

Bidimensional matrices of the irrep E_g for a set of generators of the point group 4/mmm:

$$T(4_z) = \begin{matrix} 0 & -1 \\ 1 & 0 \end{matrix} \quad T(m_x) = \begin{matrix} -1 & 0 \\ 0 & 1 \end{matrix} \quad T(-1) = \begin{matrix} 1 & 0 \\ 0 & 1 \end{matrix}$$

Table 2: Irreps of the point group mmm

Character Table										
D_{2h}(mmm)	#	1	2_z	2_y	2_x	-1	m_z	m_y	m_x	functions
A_g	Γ_1^+	1	1	1	1	1	1	1	1	x^2,y^2,z^2
B_{1g}	Γ_3^+	1	1	-1	-1	1	1	-1	-1	xy,J_z
B_{2g}	Γ_2^+	1	-1	1	-1	1	-1	1	-1	xz,J_y
B_{3g}	Γ_4^+	1	-1	-1	1	1	-1	-1	1	yz,J_x
A_u	Γ_1^-	1	1	1	1	-1	-1	-1	-1	_
B_{1u}	Γ_3^-	1	1	-1	-1	-1	-1	1	1	z
B_{2u}	Γ_2^-	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	Γ_4^-	1	-1	-1	1	-1	1	1	-1	x

Elements of the space group Pnma:

(E| 0 0 0), (2x| ½ ½ ½), (2y| 0 ½ 0) , (2z| ½ 0 ½), (-1| 0 0 0), (mx| ½ ½ ½), (my| 0 ½ 0), (mz| ½ 0 ½)

Table of the irreps for the point group $P_{\mathbf{k}}$= m2m for **k**=(0,β,0) in Pnma:

	E	2_y	m_x	m_z
τ_1	1	1	1	1
τ_2	1	-1	1	-1
τ_3	1	1	-1	-1
τ_4	1	-1	-1	1