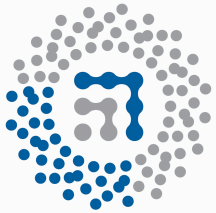


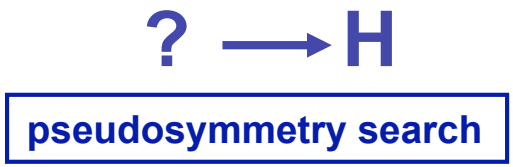
ZTF-FCT
Zientzia eta Teknologia Fakultatea
Facultad de Ciencia y Tecnología

Universidad del País Vasco
Euskal Herriko Unibertsitatea

Structural Pseudosymmetry and its applications

PSEUDOSYMMETRY SEARCH:

We know a structure with space group H and we want to know if it is close to a configuration of higher symmetry



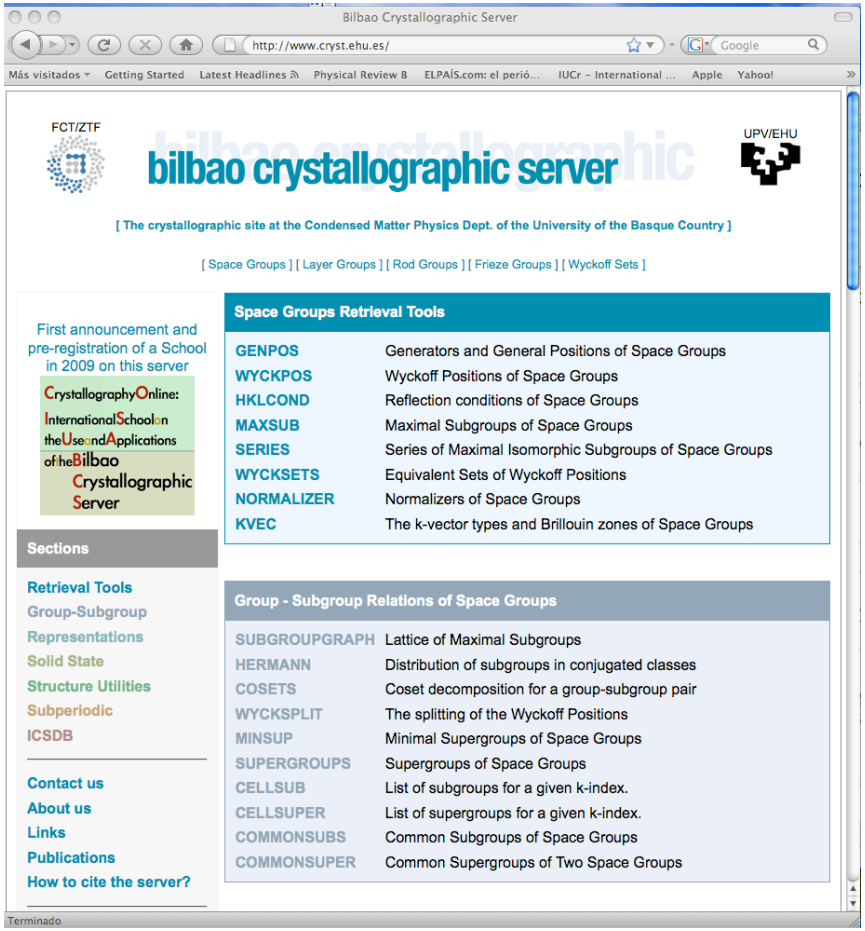
We search for a structure with space group G (supergroup of F) such that:

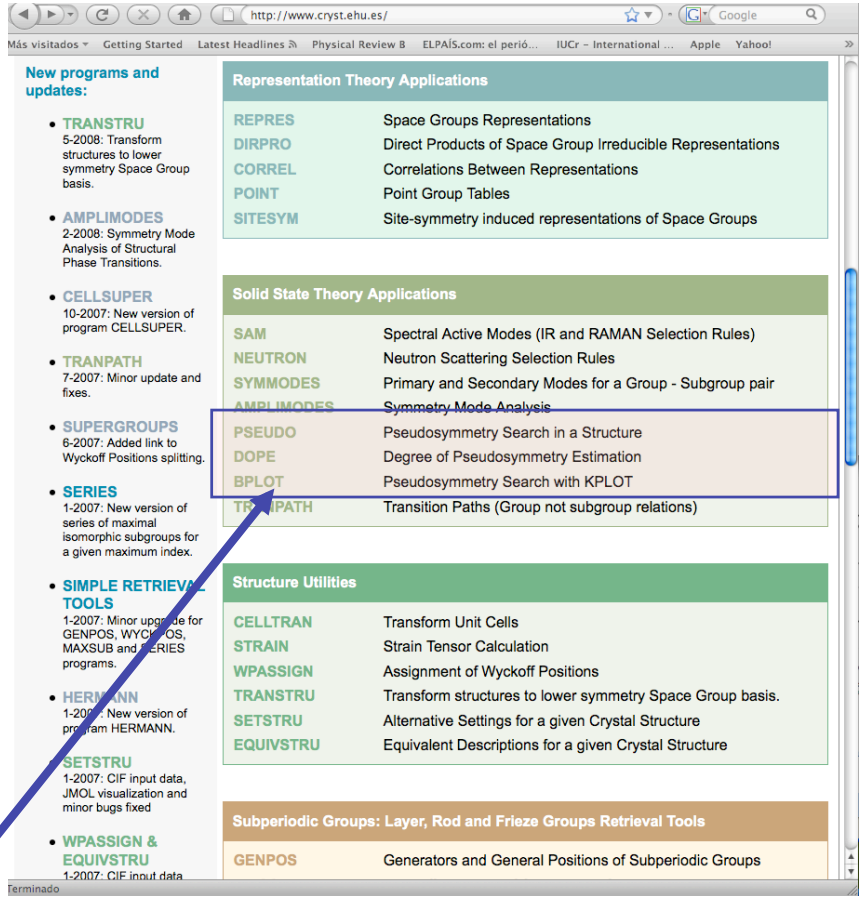
Structure G = Structure F + small (symmetry-breaking) distortion

Pseudosymmetry detection can be useful for :

- Prediction of symmetry and structure of other phases.
- Prediction of phase transitions.
- Identification of ferroic materials: ferroelectrics, ferroelastics.
- Determination of an optimized virtual parent structure.
- Detection of false symmetry assignments (overlooked symmetry).
- Identification of the symmetry of theoretical structures calculated without symmetry restrictions (ab-initio calculations).

Pseudosymmetry search in www.cryst.ehu.es:





three programs for pseudosymmetry search

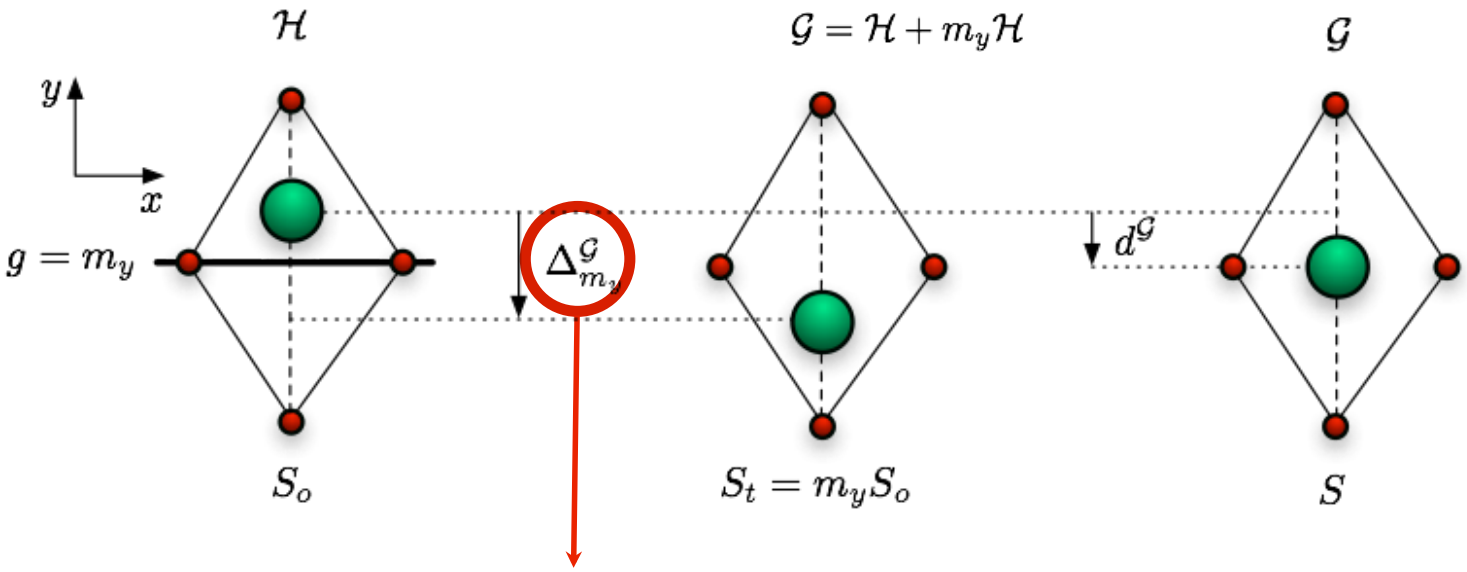
PROGRAMS FOR PSEUDOSYMMETRY SEARCH:

PSEUDO - Atomic displacement method

DOPE - Electron density method

BPLOT - KPLOT method (R. Hundt)

PSEUDO. ATOMIC DISPLACEMENTS METHOD

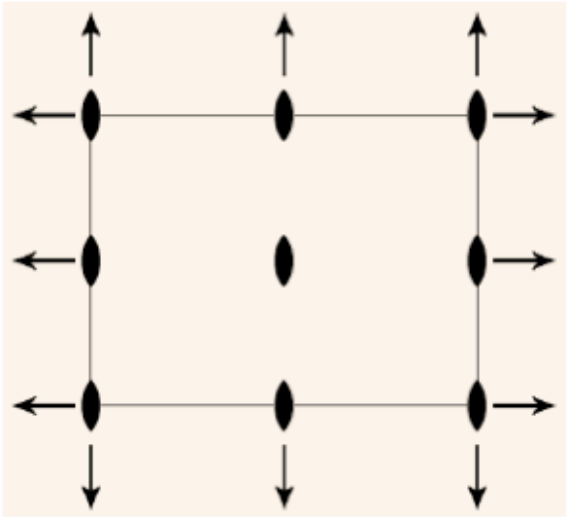


Maximal distance between all compatible atom pairings

Asumption:
The high symmetry phase is described by a supergroup of the initial space group.

$$G=H+g_2H+ \ldots +g_kH$$

Supergroups of the same type



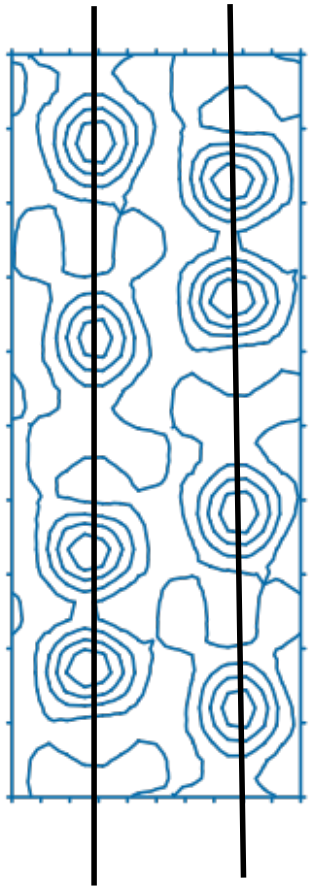
$$\mathcal{H} = \mathrm{P}\mathbf{222}$$

$$\mathcal{G} = \mathrm{P}\mathbf{422}$$

$$\mathrm{P}\mathbf{422} = \mathrm{P}\mathbf{222} + (\mathbf{4}|\boldsymbol{\omega})\mathrm{P}\mathbf{222}$$

	4 en	ω	$\mathcal{G}$
4_z	$(0,0,0)$	$(0,0,0)$	$(P422)_1$
4_y	$(0,0,0)$	$(0,0,0)$	$(P422)_2$
4_x	$(0,0,0)$	$(0,0,0)$	$(P422)_3$
4_z	$(\frac{1}{2},0,0)$	$(\frac{1}{2},\frac{1}{2},0)$	$(P422)'_1$
4_y	$(\frac{1}{2},0,0)$	$(\frac{1}{2},0,\frac{1}{2})$	$(P422)'_2$
4_x	$(0,\frac{1}{2},0)$	$(0,\frac{1}{2},\frac{1}{2})$	$(P422)'_3$

DOPE ELECTRON DENSITY METHOD



ELECTRON DENSITY

$$\rho(\mathbf{r}) = \rho_{\circ}^{\mathcal{G}}(\mathbf{r}) + \Delta\rho(\mathbf{r})$$

DEGREE OF DISSYMMETRY

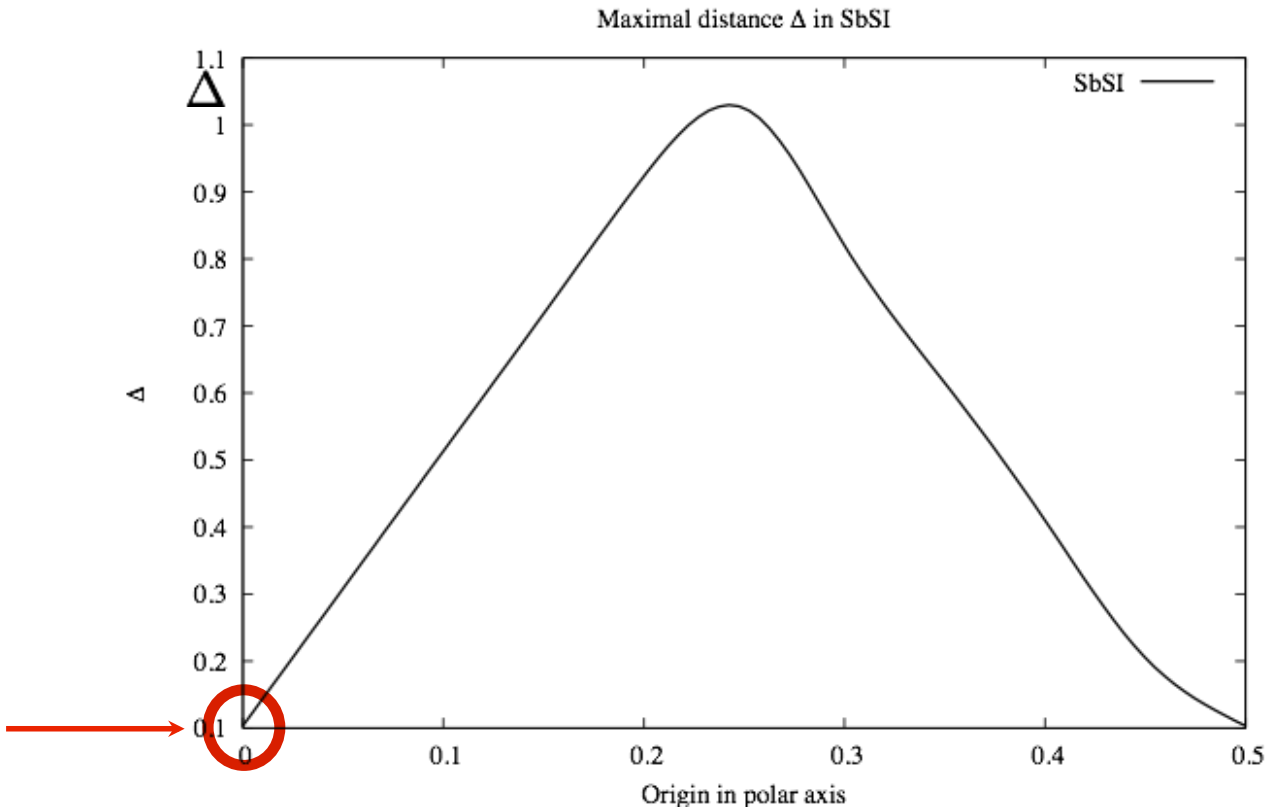
$$\gamma = \frac{\int_V |\Delta\rho(\mathbf{r})|^2 dV}{\int_V |\rho(\mathbf{r})|^2 dV}$$

DEGREE of PSEUDOSYMMETRY

$$\eta_{(W_k,\omega_k)} = \frac{\sum_{\mathbf{S}} F^*(\mathbf{S}) F(\mathbf{S}W_k) e^{2\pi i \mathbf{S}\omega_k}}{\sum_{\mathbf{S}} |F(\mathbf{S})|^2}$$

$$\gamma = 1 - \frac{1}{N}\sum_{k}^{N} \eta_{g_k}$$

THE FERROELECTRIC CASE: POLAR GROUPS



The origin in the polar axis is chosen for the minimum distance....

Search of ferroelectrics as pseudosymmetric polar structures

two necessary conditions to be a ferroelectric: (Kroumova et al. 2002)

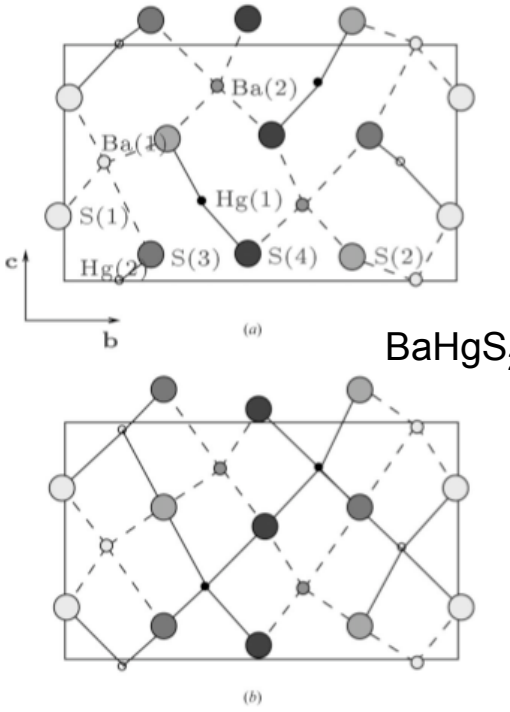
- Polar symmetry group (it should allow non-zero polarization)
- Pseudosymmetry with respect to a non-polar symmetry group – (the polar distortion should be small and “multistable”)

Pseudosymmetric structures among the compounds with symmetry $Pmc2_1$.

d^{y}_{max} is the absolute value of the maximal displacement along [010]. For a description of the remaining columns see Table 2.

Compound	$\mathcal{G}$	ε	d^{y}_{max}	d^{z}_{max}	d^{MC}_{max}	d^{rel}_{max}
(*)$(NH_2)_2CS$	*Pnma*	0.028	0.348	0.218	0.146	0.290
(*)CuAgS	*Cmcm*	0.038	0.394	0.227	0.178	0.301
(*)$CsEuNaNb_5O_{15}$	*Pmmm*	0.449	0.178	0.310	0.314	0.620
$Ca_3Mn_{1.2}Fe_{1.8}O_8$†	*Pnma*	0.478	0.223	0.343	–	0.686
$BaHgS_2$	*Pbam*	0.284	0.423	0.361	0.457	0.675
$Ca_3TiFe_2O_8$†	*Pnma*	0.460	0.347	0.421	–	0.761
Nd_4GeO_8	*Cmcm*	0.963	0.469	0.439	0.509	0.834
$Sr(OH)_2(H_2O)$	*Pnma*	0.119	0.388	0.447	–	0.895
$(Fe_{0.3}Mn_{0.7})Ta(O_2)O_2$†	*Pnma*	0.149	0	0.448	–	0.896
β-$Ba(OH)_2(H_2O)$	*Pnma*	0.088	0.404	0.468	–	0.937
$NaBa_6Nd(SiO_4)_4$	*Pnma*	−0.489	0.280	0.536	0.554	1.073
$Na(AlSi_2O_6)\ (H_2O)_{1.1}$	*Pnma*	0.467	0.666	0.551	–	0.981
$La_2Fe_{1.76}S_5$	*Pnma*	−0.008	0.099	0.677	–	1.355
CaPtP	$Pmc2_1$		0.179	0.398		0.796
$KCu(CO_3)F$	*Amm*2		0.467	0.501		1.002

† Not considered as possible ferroelectrics (see text).



$BaHgS_2$

Figure 3
Schematic projection in the plane *bc* of the polar structure with symmetry $Pmc2_1$ (*a*) and the calculated non-polar structure with symmetry *Pbam* (*b*) for $BaHgS_2$. The non-polar structure is represented with respect to the basis of the subgroup; the transformation is given in Table 3.

Known Ferroelectrics with space group $Pna2_1$

Compound	$\mathcal{G}$	$[i]$	$\Delta_{\max}$(Å)
Nb_6I_{11}	$Pccn$	2	0.547
$D_{0.45}Nb_6I_{11}$	$Pccn$	2	0.745
$NaTaO_3$	$Pnma$	2	0.232
$LaYbO_3$	$Pnma$	2	0.347
$RbGeBr_3$	$Pnma$	2	0.536
K_2SeO_4	$Pnma$	2	0.539
Cs_2BeF_4	$Pnma$	2	0.174
Rb_2BeF_4	$Pnma$	2	0.171
K_2BeF_4	$Pnma$	2	0.338
Rb_2ZnBr_4	$Pnma$	2	0.131
Rb_2ZnCl_4	$Pnma$	2	0.463
K_2ZnCl_4	$Pnma$	2	0.177
SbSI	$Pnma$	2	0.103
SbSBr	$Pnma$	2	0.109
$SbNbO_4$	$Pnna$	2	0.421
$(BiO)_4(NbO_4)Cl$	$Pbcn$	2	0.623
$CsTiO(AsO_4)$	$Pnna$	2	0.447
$KTiO(AsO_4)$	$Pnna$	2	0.610
$TlTiO(PO_4)$	$Pnna$	2	0.408

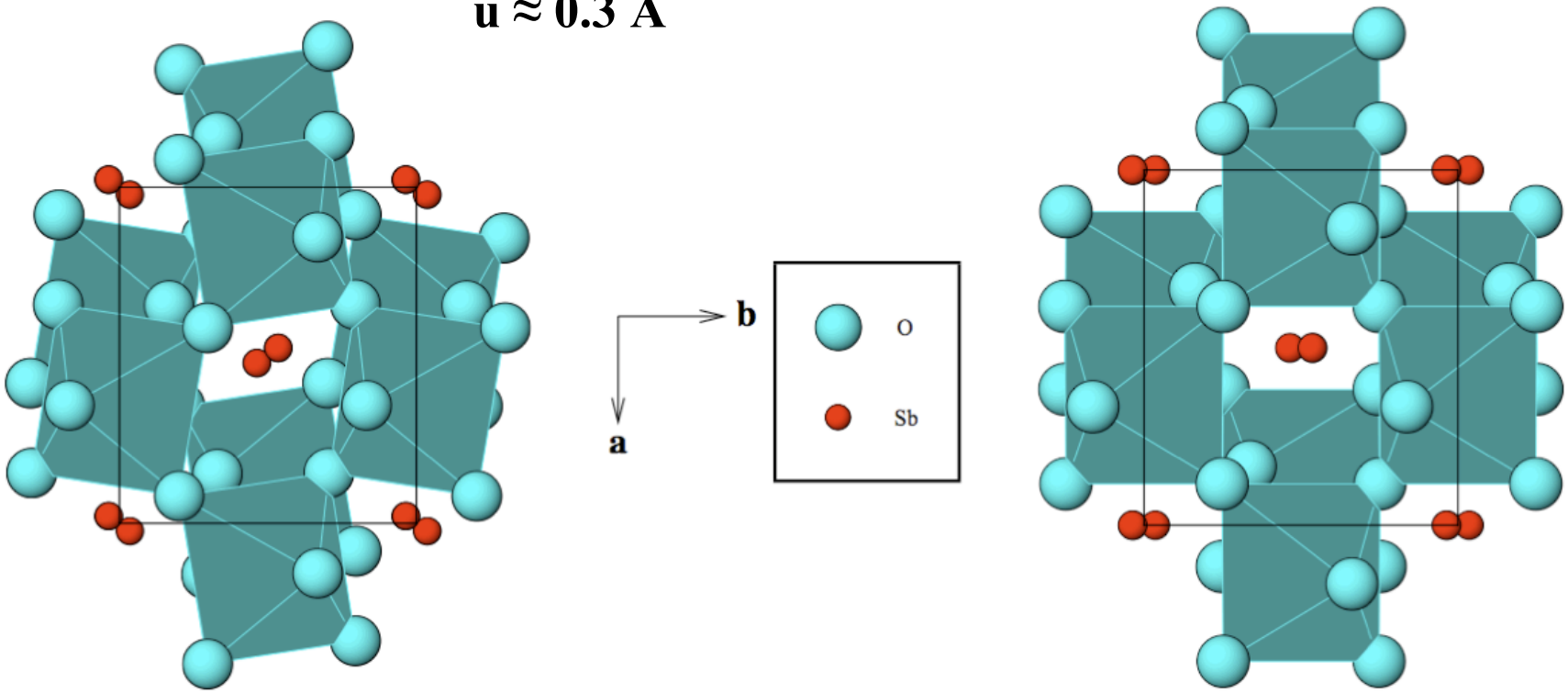
Possible Ferroelectrics with space group $Pna2_1$

Compound	$\mathcal{G}$	$[i]$	$\Delta_{\max}$(Å)
Sb_2O_4	$Pnna$	2	0.581
PbNCN	$Pnma$	2	0.193
$NaIO_3$	$Pnma$	2	0.194
$YScS_3$	$Pnma$	2	0.179
$CeSiP_3$	$Pnma$	2	0.648
$SmBeF_4$	$Pnma$	2	0.325
K_3AsS_4	$Pnma$	2	0.227
WPO_5	$Pnma$	2	0.457
$Sr_3Sb_4S_9$	$Pnma$	2	0.230
$Be_4Pr_9O_{20}$	$Pnma$	2	0.246
$Ca_{0.84}Sr_{1.16}SiO_4$	$Pnma$	2	0.580
$Tl_{1.1}AlSiO_4$	$Pnma$	2	0.590
$Na_2UO_2P_2O_7$	$Pnma$	2	0.559
$TlSnPS_4$	$Pnma$	2	0.488

Example: Sb_2O_4 $(Pna2_1 \overset{(2)}{\rightarrow} Pnna)$

$$\Delta = 0.581\text{Å y } \eta_g = 0.641\text{Å}$$

u ≈ 0.3 Å



Search of maximal pseudosymmetry through a chain of minimal supergroups:

(stepwise detection of pseudosymmetry for successive minimal supergroups)

If a structure of symmetry H is pseudosymmetric for a supergroup G, it will be pseudosymmetric for all intermediate subgroups Hi: G > ..> Hi >...> H