Crystallography Online: Workshop on the use and applications of the structural tools of the Bilbao Crystallographic Server

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EXERCISES

Crystal-structure tools & relationships

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1 Crystal structure tools

Structure data for the exercises:

http://www.cryst.ehu.es/resources/oviedo2018/StructureTools.txt

- **Exercise** 1.1. Structure descriptions for different space-group settings (Wondratschek, 2002)

  (a) In R. W. G. Wyckoff, *Crystal structures*, vol. **II**, Ch. VIII, one finds the important mineral zircon $ZrSiO_4$ and a description of its crystal structure. Many rare-earth phosphates, arsenates, and vanadates belong to the same structure type.

  Structural data: Space group $I4_1/amd = D_{4h}^{19}$, No. 141;
  lattice constants a = 6.60 Å; c = 5.88 Å.

  The origin choice is not stated explicitly. However, Wyckoff's *Crystal Structures* started to appear in 1948, when there was one conventional origin only (the later ORIGIN CHOICE 1, *i. e.* **Origin** at $\bar{4}m2$).

  $Zr:$ (a) $0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{4};\ \frac{1}{2}, 0, \frac{3}{4};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2};$
  $Si:$ (b) $0, 0, \frac{1}{2};\ 0, \frac{1}{2}, \frac{3}{4};\ \frac{1}{2}, 0, \frac{1}{4};\ \frac{1}{2}, \frac{1}{2}, 0;$
  $O:$ (h) $(0, u, v;\ 0, \bar{u}, v;\ u, 0, \bar{v};\ \bar{u}, 0, \bar{v};\ 0, \frac{1}{2}+u, \frac{1}{4}-v;\ 0, \frac{1}{2}-u, \frac{1}{4}-v;$
  $\qquad \bar{u}, \frac{1}{2}, v+\frac{1}{4};\ u, \frac{1}{2}, v+\frac{1}{4};)$ [and the same with $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})+$].

  The parameters u and v are listed with $u = 0.20$ and $v = 0.34$.

  (b) In the *Structure Reports*, vol. **22**, (1958), p. 314 one finds:

  'a = 6.6164(5) Å, c = 6.0150(5) Å'
  'Atomic parameters. Origin at center $(2/m)$ at $0, \frac{\bar{1}}{4}, \frac{1}{8}$ from $\bar{4}m2$.'
  'Oxygen: $(0, y, z)$ with $y = 0.067$, $z = 0.198$.'

  Compare the two structure descriptions and check if they belong to the same structure type. Which of the structure tools of the Bilbao Crystallographic Server could help you to solve the problem?

  *Hint:*In order to compare the different data, the parameters of Wyckoff's book are to be transformed to 'origin at center $2/m$', *i. e.* ORIGIN CHOICE 2.

- **Exercise** 1.2. Equivalent structure descriptions

  $P(C_6C_5)_4[MoNCl_4]$ is tetragonal, space group $P4/n$, with the following co-ordinates:

Atom	Wyckoff position	Coordinate x	triplets y	z	
P	2b	0.25	0.75	0	
Mo	2c	0.25	0.25	0.121	
N	2c	0.25	0.25	−0.093	(H and C3 to C6 omitted)
C1	8g	0.362	0.760	0.141	
C2	8g	0.437	0.836	0.117	
Cl	8g	0.400	0.347	0.191	

  How many equivalent sets of co-ordinates can be used to describe the structure? What are their co-ordinates?

Hint: The number of different equivalent descriptions of $P(C_6C_5)_4[MoNCl_4]$ is equal to the index of its space group $P4/n$ in the Euclidean normalizer. The different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group. In the special case of $P(C_6C_5)_4[MoNCl_4]$ such equivalent descriptions can be generated, for example, by the translations $t(0,0,1/2)$ and $t(1/2,1/2,0)$, and by a reflection through a mirror plane at (x,x,z) represented by the coordinate triplet (y,x,z).

- **Exercise** 1.3. Isoconfigurational structure types (Koch & , Fischer, 2002)

  Do the following three structures belong to the same structure type? Try to find analogous coordinate descriptions for all three crystal structures.

  1. $KAsF_6$ (ICSD: 59413)
     Unit Cell   7.348(1)   7.348(1)   7.274(8)   90. 90. 120
     Space group   R-3h

Atom	Wyckoff position	Coordinate x	triplets y	z
K	3b	0.33333	0.66667	0.166667
As	3a	0	0	0
F	18f	0.1292(2)	0.2165(2)	0.1381(2)

  2. $BaIrF_6$ (ICSD: 803188)
     Unit Cell   7.3965(1)   7.3965(1)   7,2826(1)   90. 90. 120
     Space group   R-3h

Atom	Wyckoff position	Coordinate x	triplets y	z
Ba	3b	0.33333	0.6666	0.166666
Ir	3a	0	0	0
F	18f	0.0729(2)	0.2325(2)	0.1640(2)

  3. $BaSnF_6$ (ICSD: 33788)
     Unit Cell   7.4279(2)   7.4279(2)   7.418(2)   90. 90. 120
     Space group   R-3h

Atom	Wyckoff position	Coordinate x	triplets y	z
Ba	3a	0	0	0
Sn	3b	0	0	0.5
F	18f	0.2586(3)	0.8262(3)	0.0047(3)

  Hint: Consider the Euclidean normalizer of symmetry group $R\bar{3}$(hex) of $KAsF_6$. The number of different equivalent descriptions of $KAsF_6$ is equal to the index of its space group in the Euclidean normalizer. The different descriptions are generated by the coset representatives of the decomposition of the normalizer with respect to the space group. In the special case of $KAsF_6$ such equivalent descriptions can be generated, for example, by the translation $t(0,0,1/2)$, by a reflection through a mirror plane at $(x,-x,z)$ represented by the coordinate triplet $(-y,-x,z)$, etc.

- **Exercise** 1.4.   Crystal structure descriptions

  In Inorganic Crystal Structure Database can be found several structure data sets of ϵ-Fe_2O_3, all of them of symmetry $Pna2_1$ (No.33). Compare the two structure descriptions listed in the *Exercise Data* file and check if they belong to the same structure type.

2 Symmetry relations between crystal structures

Structure data for the exercises:

http://www.cryst.ehu.es/resources/oviedo2018/StructureRelationships.txt

- **Exercise** 2.1. Cristobalite phase transitions

  At low temperatures, the space-group symmetry of cristobalite is given by the space group is $P4_12_12$ (92) with lattice parameters $a = 4.9586\text{Å}$, $c = 6.9074\text{Å}$. The four silicon atoms are located in Wyckoff position $4(a)..2$ with the coordinates $x, x, 0; -x, -x, 1/2; 1/2 - x, 1/2 + x, 1/4; 1/2 + x, 1/2 - x, 3/4$, $x = 0.3028$. During the phase transition, the tetragonal structure is transformed into a cubic one with space group $Fd\bar{3}m(227)$, $a = 7.147A$. It is listed in the space-group tables with two different origins.

  1. If Origin choice 2 setting is used (with point symmetry $\bar{3}m$ at the origin), then the silicon atoms occupy the position $8(a)$ $\bar{4}3m$ with the coordinates 1/8, 1/8, 1/8; 7/8, 3/8, 3/8 and those related by the face - centring translations. Describe the structural distortion from the cubic to the tetragonal phase by the determination of (i) the displacements if the Si atoms in relative and absolute units, and (ii) the lattice distortion accompanying the transition.

  2. Repeat the calculations for the characterization of the phase transition using the *Origin-choice 1* description of the high-symmetry phase (*cf. Exercise Data* file for the structure data).

- **Exercise** 2.2. Ferroelastic phase transitions

  (a) Lead phosphate $Pb_3(PO_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R\bar{3}m$ (No.166) to a ferroelastic phase of symmetry $C2/c$ (No.15). Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server*:

    (a) characterize the symmetry reduction between the high- and low-symmetry phases (index and transformation matrix);

    (b) describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.

  (b) Lead phosphate-vanadate $Pb_3(PVO_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R\bar{3}m$ (No.166) to a ferroelastic phase of symmetry $P2_1/c$ (No.14). Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server* describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.

- **Exercise** 2.3. CoU hettotype of the $\beta-$brass structure

  Show that the crystal structure of CoU maybe interpreted as a slightly distorted CsCl (or $\beta-$brass, CuZn)-type structure. Using the structural data in the *Exercise Data* file, characterize the structural relationship between the CoU structure and CsCl structure.

- **Exercise** 2.4. Structural pseudosymmetry of Pb_2MgWO_6

  Analyse the structural pseudosymmetry of Pb_2MgWO_6 using the program `PSEUDO`, *cf.* structure data in *Exercise Data* file: (i) Try to determine the maximal possible preudosymmetry stepwise, *i.e. climbing* via the minimal supergroups (applying Option 1 of the program); (ii) Apply Option

3 of `PSEUDO` (Pseudosymmetry search for a specific supergroup given by a transformation matrix $(\boldsymbol{P}, \boldsymbol{p})$) to confirm the flagged maximal pseudosymmetry in (i).

- **Exercise** 2.5.   Structural pseudosymmetry of a $C222_1$ structure

  Using the program `PSEUDO`, Option1, analyse the structural pseudosymmetry of a hypothetical $C222_1$ (No. 20) structure stepwise, *i.e. climbing* via the minimal supergroups (*cf.* structure data in *Exercise Data* file). Compare the results if different minimal-supergroup paths are followed.

- **Exercise** 2.6.   Apparently complex phase Ga-II of Ga under pressure

  Analyse the structural pseudosymmetry of the orthorhombic phase Ga-II of Ga under pressure using the program `PSEUDO` (structure data in *Exercise Data* file).

  Hint: As a first step check the structural pseudosymmetry with respect to an isomorphic supergroup of index 13 (can you guess why?), specified by the transformation matrix: **a**,**b**,13**c**, Option 3.

- **Exercise** 2.7.   Non-polar phases of $NaSb_3F_{10}$

  The compound $NaSb_3F_{10}$ whose room-temperatute phase is polar, space group $P6_3$, has been predicted to be ferroelectric (*cf.* structure data in *Exercise Data* file). The symmetries $P6_322$ and $P6_3/mmc$ had been proposed for two successive non-polar phases at high temperature. Applying the pseudosymmetry approach confirm the predictions for the non-polar phases of $NaSb_3F_{10}$. Show that apart from $P6_322$ phase, there are two more appropriate candidates for the intermediate phases between the polar phase $P6_3$ and the non-polar one of maximal symmetry, $P6_3/mmc$.