

Hands-on exercises on the use of AMPLIMODES

A1. Polar modes depend on the origin choice. Knowledge of a parent phase is not necessary

$\text{S}_2\text{Sn}_2\text{P}_6$ has a monoclinic $\text{P}2_1/c$ phase at high temperatures (J. Sol. State Chem. (1992) 96, 294) and a ferroelectric non-centrosymmetric phase of symmetry Pc at low temperatures (Z. Naturf. B. (1974) 29, 312-317) :

```
14
6.5500 7.4930 11.3157 90.00 124.19 90.00
5
Sn 1 4e -0.2842 0.3692 -0.2431
P 1 4e 0.3723 0.3914 -0.0671
S 1 4e 0.1362 0.4975 -0.2629
S 2 4e 0.21 0.309 0.0328
S 3 4e 0.5988 0.1976 -0.057

7
6.513000 7.488000 11.309900 90.000000 124.000000 90.000000
10
Sn 1 2a 0.304600 0.385600 0.277000
Sn 2 2a 0.740900 0.124500 0.777900
P 1 2a 0.372800 0.860800 0.433600
P 2 2a 0.626600 0.644700 0.567400
S 1 2a 0.140700 0.751100 0.239800
S 2 2a 0.203800 0.946200 0.528800
S 3 2a 0.602100 0.051700 0.444200
S 4 2a 0.865200 0.743700 0.764900
S 5 2a 0.785900 0.563300 0.464700
S 6 2a 0.402500 0.448000 0.555000
```

i) Obtain with AMPLIMODES that the ferroelectric structure has two distortion modes, a primary one that yields the Pc space group, i.e. the order parameter distortion, and a secondary one compatible with the parent symmetry. (Choose that AMPLIMODES shifts the origin of the polar distorted phase). Which atoms are moving more strongly in the transition? [The transformation matrix between the settings of the two groups includes an origin shift of $(0 \frac{1}{4} 0)$. This can be obtained for instance using the program SUBGROUPGRAPH]

ii) Let us change now arbitrarily some of the coordinates of the parent $\text{P}2_1/c$ structure displacing the positions by some small amount (below 1 Å):

```
#"Wrong Parent Structure"
14
6.5500 7.4930 11.3157 90.00 124.19 90.00
5
Sn 1 4e -0.3 0.38 -0.27
P 1 4e 0.33 0.36 0.07
S 1 4e 0.1 0.52 -0.23
S 2 4e 0.25 0.33 0.1
S 3 4e 0.6 0.15 -0.1
```

Apply AMPLIMODES, increasing now the default tolerance Δ to 2 Å. Check the result choosing that AMPLIMODES shifts the origin, and then without shifting. Check that if the shift is done, the primary polar distortion does not change, while the secondary one, compatible with the parent symmetry, changes drastically. (Conclusion: symmetry

mode analysis can be done even without knowing the structure of the parent phase...)

A2. Secondary modes can be negligible reducing the number of degrees of freedom.

NbS₃ is triclinic with space group P-1 (N. 2), but belongs to a family where most of the compounds have P2₁/m (N. 11) symmetry and their cell parameter along b is approximately half the value. NbS₃ has a small distortion with respect to this monoclinic structural model common to the family. A virtual parent structure of P2₁/m can be easily postulated for NbS₃ from this knowledge [it can also be derived using the program PSEUDO of the Bilbao crystallographic server that detects pseudosymmetry and builds-up the configuration of higher symmetry closer to the observed one]:

```
11
4.963 3.365 9.144 90. 97.17 90.
4
Nb 1 2e 0.715500 0.75000 0.348650
S 1 2e 0.763400 0.25000 0.553550
S 2 2e 0.878850 0.25000 0.169450
S 3 2e 0.466950 0.25000 0.174150
```

The experimental P-1 structure is in the CIF file provided. The transformation matrix between the settings of the two groups must include the duplication of the b parameter, but does not require an origin shift. (*file required: icsd_NbS3.cif*)

i) Apply AMPLIMODES to obtain the mode decomposition. Observe that while the structure has 24 free parameters, the distortion is dominated by an irrep distortion that is determined by only 12 parameters. Check the amplitude of the full symmetric GM1+ distortion (why is it zero?). Compare the polarization vectors of the two irrep distortions.

ii) Using one of the different possibilities available, obtain a graphical representation of the irrep distortion modes in NbS₃.

A3. Comparison of polarization vectors: detection of a false minimum

BaMnO₃ has been determined at 1.7K and at 80K (*Chem. Mater.* 12 (2000) 831-838) with space group P63cm. The structure at room temperature is also known and has a higher symmetry: P63/mmc. The CIF files of the three structures are attached (*the icsd CIF files have been modified introducing 6 digits for 1/3 and 2/3 values!*). The relation between the settings of the two symmetries can be chosen as (**a+2b**, **-2a-b**, **c**; 0 0 0).

i) Decompose with AMPLIMODES the 80K structure into symmetry-adapted modes with respect to the parent phase. Identify the primary dominant distortion. Try to understand and characterize this dominant mode.

ii) How many positional atomic parameters are necessary to refine this structure and how many are required to describe the dominant primary distortion?

iii) Apply AMPLIMODES to the 1.7K structure. Compare the results with those of the structure at 80K. First, compare the total amplitudes for each irrep distortion mode, and check if the result is plausible. Second compare the polarization vectors of each

distortion mode, by inspection, and then by calculating their dot products. You should detect that there is some inconsistency in one of the models for one of the secondary modes (the atomic displacements of this secondary mode are more or less opposite in the two models, relative to those of the primary mode). So probably one of the structures is probably wrong (corresponding to a false minimum in the refinement).

(files required: icsd_parent_BaMnO3.cif, icsd_BaMnO3_80K.cif, icsd_BaMnO3_1.7K.cif)