QUESTIONNAIRE FOR the
STRUCTURE DETERMINATION BY POWDER DIFFRACTOMETRY ROUND ROBIN - 3

Questionnaire completed for **sample 2** by Esther C. Schilder and Jaap N. Louwen, Albemarle Catalysts Amsterdam.

It is advised to complete the form as the structure determination progresses.

O.0 Precise date of
     - data download   : ex : Fri, 14 Feb 2008 17:28
     - results submission : Thu, 03 April 2008

0.2 Is the second sample structure solvable with this quality of data ?   Yes [X] No [ ]

Although we are not completely confident since the thermal displacement parameters of some of the atoms refine to negative values when left unconstrained.

Then, for sample 2:

1. Preliminary work

  1.1 Did you obtain additional information ?
We found a paper by Kovalevsky et al (Materials Letters 38 (1999) 300-304) that discusses what appears to be the same material as that used for recording the scans. They call it "hexagonal $La_2W_{1.25}O_{6.75}$". They mention the space group R-62c. Since that one does not exist, we assumed P-62c was intended and used that group in the extraction of intensities from the synchrotron X-ray pattern.

  1.2 Did you obtain additional information from the
     powder pattern ?   No

  1.3 Did you extract the structure factors ?   Yes [X] No [ ] From the X-ray scan

     1.3.1 If yes, which program(s) did you use ? TOPAS-R, version 3
     1.3.2 Give the angular range: 4 - 45.5
     1.3.3 Give the number of extracted structure factors: 1055
     1.3.4 Give the Rp and Rwp (conventional Rietveld, background subtracted): 12.8/15.6
     1.3.5 Give the Rp and Rwp (background not subtracted): 7.7/10.2

     1.3.6 If not, did you use the whole pattern ?
Yes for both the neutron and the X-ray scan

     1.3.8 If you use the whole or a partial pattern, did you keep fixed the
        profile parameters?

Note quite. The neutron pattern was used in simulated annealing (see below). It is very undesirable to include the profile (or unit cell or background, etc.) parameters in that procedure. So, they were first derived by what is called an hkl phase fit in TOPAS (Pawly or LeBail method) and then fixed for simulated annealing. However, each time some significant progress was achieved in SA, unit cell, background and profile as well as sample displacement parameters were refined with the current structural model (for both the X-ray and the neutron scan)

2- Structure solution

2.1 Did you use direct methods ?　　　　　Yes [ ]　No [X]

2.2 Did you use Patterson methods ?　　　　Yes [ ]　No [X]

2.3 Did you use another method ?　　　　　Yes [X]　No [ ]

We used both Charge Flipping (to locate the heavy atoms) and a direct space method (to locate the oxygen atoms)

　　2.3.2 Which program(s) did you use (name and reference) ?
We used Lukáš Palatinus' program superflip, the version enhanced with the histogram method (Baerlocher, C., McCusker, L. and Palatinus, L. (2007), 'Charge flipping combined with histogram matching to solve complex crystal structures from powder diffraction data', Z. Kristalogr. 222, 47–53) for CF.
We used Bruker TOPAS-R version 3 for simulated annealing (direct space method).
EXPGUI/GSAS was used for refinements.

　　2.3.3 If you used direct space methods, how many independent
　　　　molecules did you use (give details on these molecules)? How
　　　　many degrees of freedom (total) ? How many torsion angles ?

By the time we started using the direct space method we had found that the most probable structure model had 18 W and 36 La ions in the unit cell, which implied 108 oxygen ions. Superflip had indicated P-62c as the most likely space group. Since the general position in SG190 has a multiplicity of 12, we started by assuming all oxygen ions to occupy general positions, meaning that 108/12=9 oxygen atom positions needed to be determined. This means we used 27 degrees of freedom. This number is a little too large for comfort and we got stuck in what was obviously a local minimum (some very short O-O distances were observed). We found the following procedure to work well for getting out of such a false solution:
- Using the current structure, refine O occupation numbers
- Fix the coordinates of the atoms that refined to an occupation around 1, Reset all occupation numbers to 1.
- Restart the simulated annealing.
The degrees of freedom are now restricted to the coordinates of the atoms that are obviously not in a valid position.
Note that we used both the neutron and the X-ray scan in simulated annealing, though possibly just the neutron scan might have been sufficient.

　2.4 Did you first locate the whole structure ?　Yes [ ]　No [X]

　　2.4.1 If not, how many atoms did you locate ?　　　54 on 9 symmetry unique positions
　　2.4.2 Give their name and initial atomic coordinates
　　　　　Atom　　x　　　y　　　z

Atom	x	y	z
W1	0.0	0.0	0.41591
W2	0.66667	0.33333	0.33418
W3	0.33333	0.66667	0.50370
W4	0.0	0.0	0.25
W5	0.33333	0.66667	0.36555
La1	0.9640	0.2415	0.66773
La2	0.5749	0.9570	0.58458
La3	0.9447	0.5716	0.25
La4	0.2569	0.0	0.0

2.4.3 Were the initial atomic coordinates taken from a known
structure ?   Yes [ ] No [X]

We ran the Charge Flipping procedure on the intensities extracted from the X-ray scan using the histogram method (histogram generated from a random structure based on the assumed stoichiometry $La_{32}W_{20}O_{108}$). The resulting density map showed 58 maxima. W atoms were placed on all symmetry unique positions and we refined W positions and occupation numbers against the X-ray scan (using EXPGUI/GSAS). Of the 58 positions suggested by charge flipping, 4 refined to almost zero occupation, 18 refined to an occupation roughly about 1 and 36 refined to an occupation factor around 0.7. This suggested $La_{36}W_{18}$ and this stiochiometry was refined. It was obviously different from our assumed stiochiometry, but since Ln_2WO_6 (Ln=lanthanide) structures are quite common the derived stiochiometry was credible.

3- Structure completion

  3.1 Did you perform Fourier difference syntheses before
      refining the structure by the Rietveld method ? Yes [ ] No [X]

  3.5 Did you made first Rietveld refinements without preliminary
      Fourier difference syntheses ?   Yes [ ] No [X]

4- Final refinement

     - Give the final atomic coordinates, thermal parameters,
       standard deviations, Reliability factors...........
                 Atom   x   y   z   B
loop_
    _atom_site_label
    _atom_site_fract_x
    _atom_site_fract_y
    _atom_site_fract_z
    _atom_site_occupancy
    _atom_site_thermal_displace_type
    _atom_site_U_iso_or_equiv
    _atom_site_symmetry_multiplicity

Atom	x	y	z	occ	type	U_iso	mult
W1	0.0	0.0	0.41637(17)	1.0	Uiso	0.00077(7)	4
W2	0.66667	0.33333	0.33432(13)	1.0	Uiso	0.00077(7)	4
W3	0.33333	0.66667	0.50395(11)	1.0	Uiso	0.00077(7)	4
W4	0.0	0.0	0.25	1.0	Uiso	0.00077(7)	2
W5	0.33333	0.66667	0.36545(12)	1.0	Uiso	0.00077(7)	4
La1	0.96647(24)	0.24038(28)	0.66787(12)	1.0	Uiso	0.00077(7)	12
La2	0.57515(31)	0.96061(26)	0.58407(10)	1.0	Uiso	0.00077(7)	12
La3	0.9419(4)	0.5719(5)	0.25	1.0	Uiso	0.00077(7)	6
La4	0.2562(5)	0.0	0.0	1.0	Uiso	0.00077(7)	6
O1	0.1794(6)	0.1604(6)	0.28840(19)	1.0	Uiso	0.00077(7)	12
O2	0.9711(6)	0.8222(7)	0.95126(19)	1.0	Uiso	0.00077(7)	12
O3	0.1716(6)	0.1444(6)	0.37788(18)	1.0	Uiso	0.00077(7)	12
O4	0.1763(7)	0.4965(6)	0.86822(19)	1.0	Uiso	0.00077(7)	12
O5	0.1833(7)	0.4940(6)	0.70585(20)	1.0	Uiso	0.00077(7)	12
O6	0.7122(6)	0.5259(7)	0.89413(18)	1.0	Uiso	0.00077(7)	12
O7	0.5163(6)	0.3743(6)	0.67466(20)	1.0	Uiso	0.00077(7)	12
O8	0.4783(6)	0.1888(7)	0.45458(17)	1.0	Uiso	0.00077(7)	12
O9	0.1473(6)	0.5952(6)	0.47621(20)	1.0	Uiso	0.00077(7)	12

```
Restraint data statistics:
No restraints used

Powder data statistics                  Fitted          -Bknd            Average
                  Bank Ndata Sum(w*d**2) wRp    Rp      wRp    Rp      DWd  Integral

Hstgm  1 PXC   1 13166  33554.     0.1575 0.1231 0.1617 0.1325  0.330  0.953
Hstgm  2 PNC   1  2795  25637.     0.1044 0.0808 0.1120 0.0846  0.091  0.962
Powder totals    15961  59191.     0.1264 0.0963 0.1340 0.1012  0.227
Cycle 444 There were  15961 observations.
Total before-cycle CHI**2 (offset/sig) = 5.9191E+04 ( 2.4303E+02)

Reduced CHI**2 =  3.727     for    81 variables
Histogram  1  Type PXC   Nobs = 1062 R(F**2) =  0.2087
Histogram  2  Type PNC   Nobs =  949 R(F**2) =  0.1029
Marquardt factor for this cycle =    4.91

   1 Columns of the    81 Column matrix are 0.0

CPU times for matrix build     1.56 sec; matrix inversion     0.02 sec
Final variable sum((shift/esd)**2) for cycle 444:     0.49 Time:   1.58 sec
STOP GENLES terminated successfully statement executed

D:\store\GSASBoth>pause
Press any key to continue . . .
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- Give details about constraints, restraints
-

We constrained all thermal displacement parameters (Uiso) to the same value. The reason is that the Usio values for the W ions consistently refined to negative values. Obviously, this is something to worry about. Yet the fit obtained to the two scans is satisfactory and the interatomic distances and angles look reasonable too. Either we are wrong, or there is considerable disorder in the structure (or there is some experimental issue, but corrections for preferred orientation and adsorption in GSAS did not improve things – and were also not very significant).

5- Feel free to add any intermediate results (list of extracted structure factors, software decisive input and output data...) or comments you might consider as essential (details on hardware, time for solving the structure, number of moves by Monte Carlo or molecule position trial, any picture...).

A .cif file, generated by GSAS, has been included in the submission .zip folder.