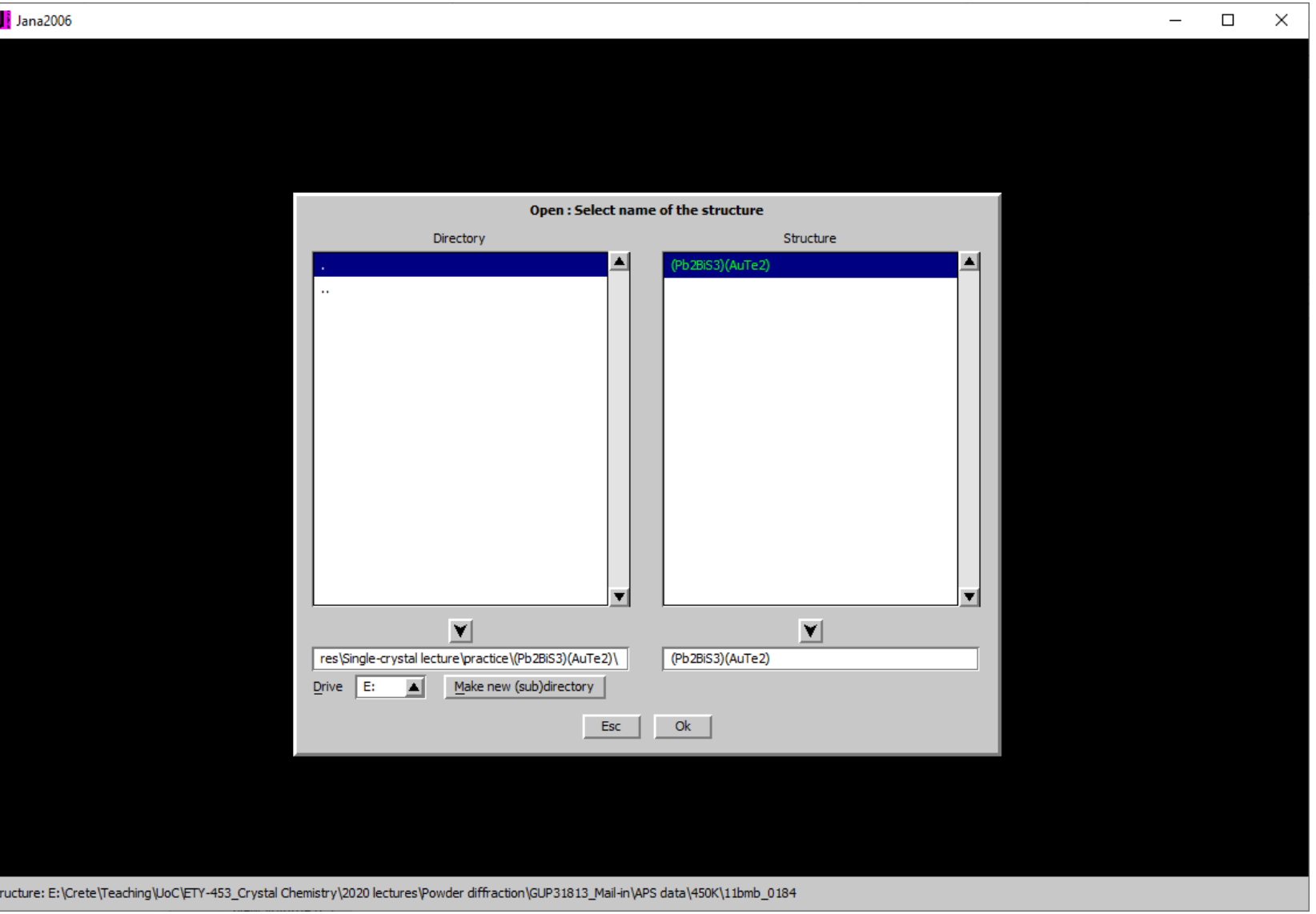
Structure Determination Using Jana2006

Structural Analysis from Single-Crystal and Powder X-ray data

Import your data

Find your data from data reduction and place them in a separate folder

Start a new structure from the File -> Structure menu



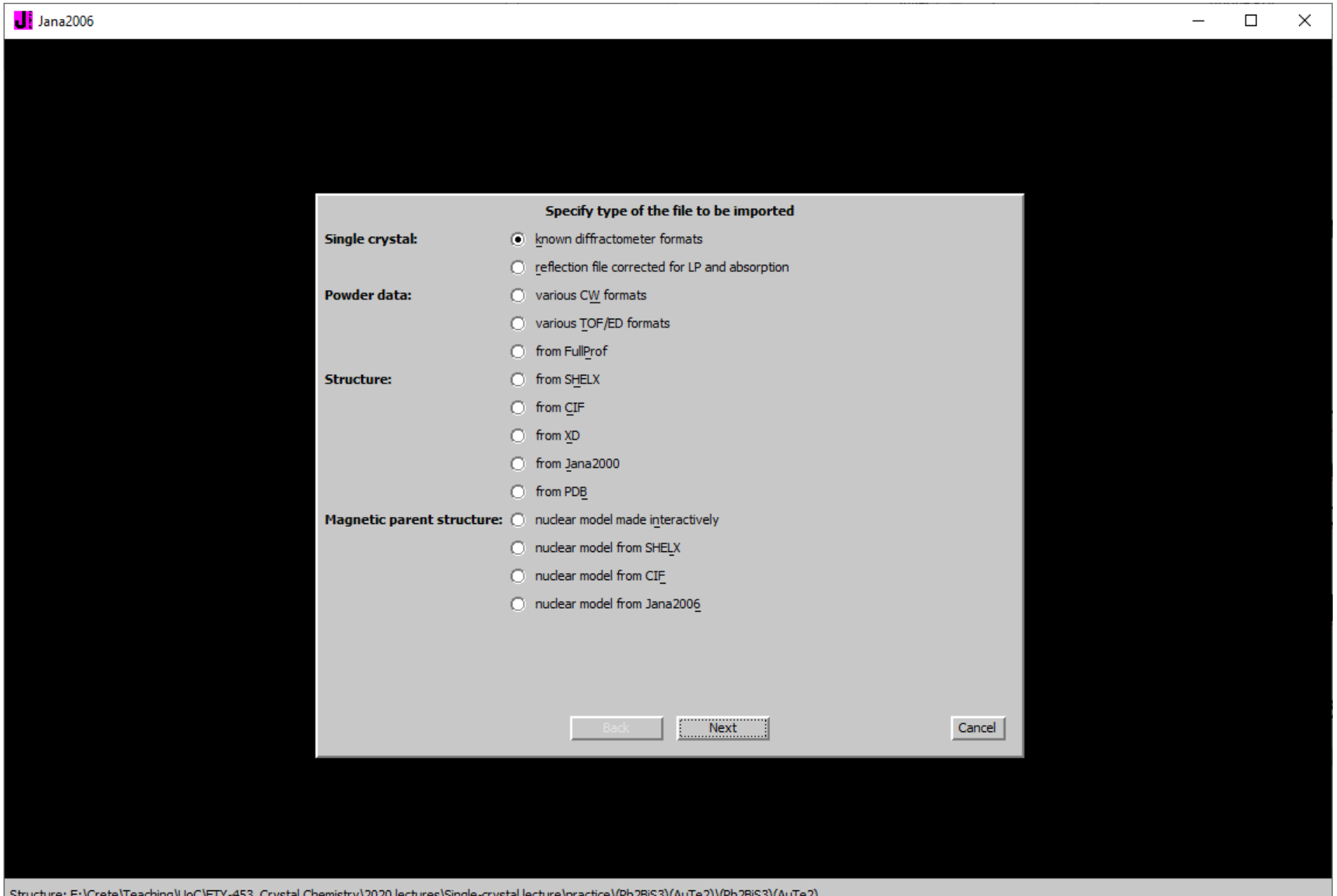
File formats:

1) hkl + sum files (STOE)
2) hkl + p4p files (Bruker)
3) hkl + cif_od files (Rigaku)

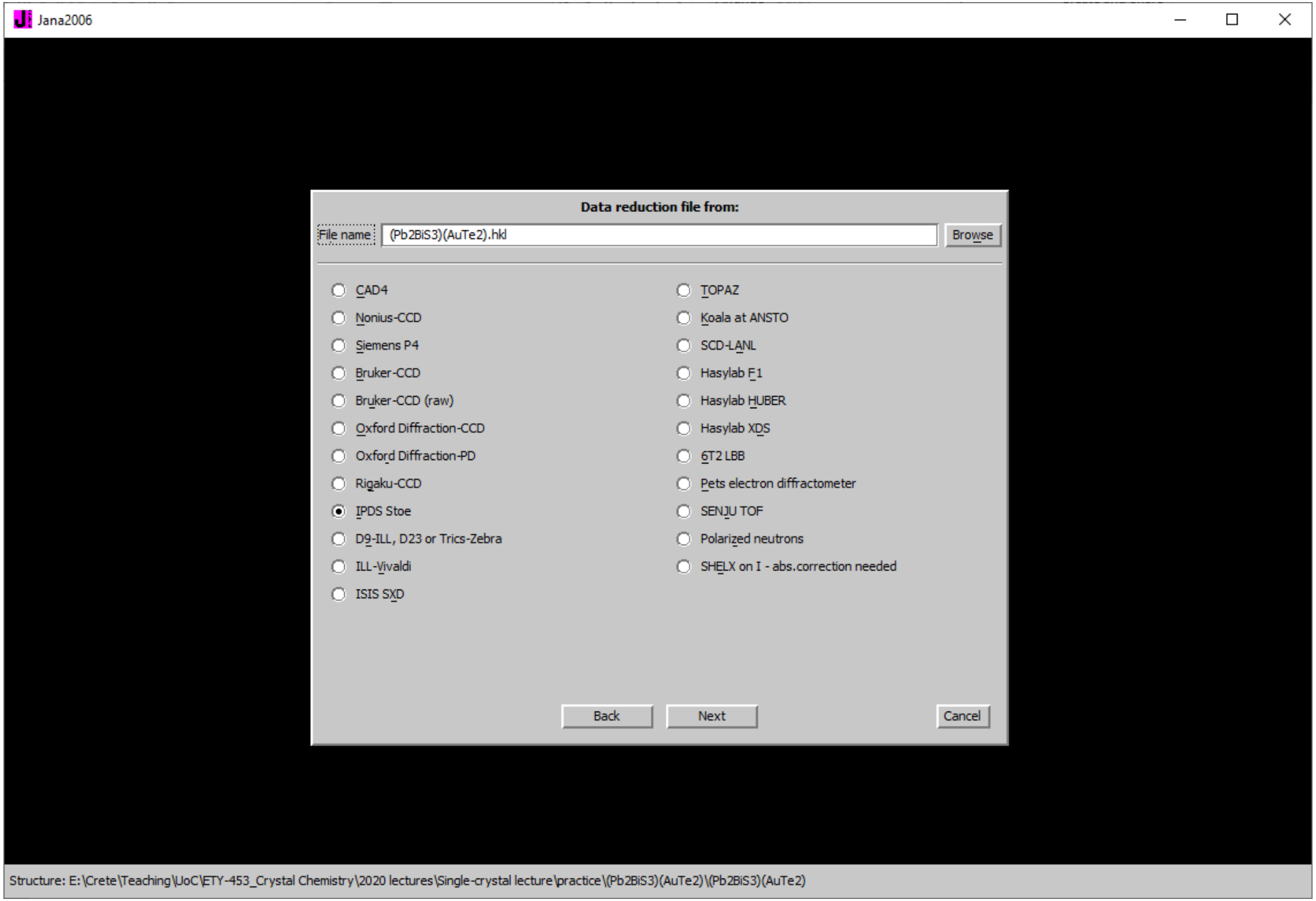
4) hkl from powder data…

… you should already be there from pattern matching (LeBail fitting)

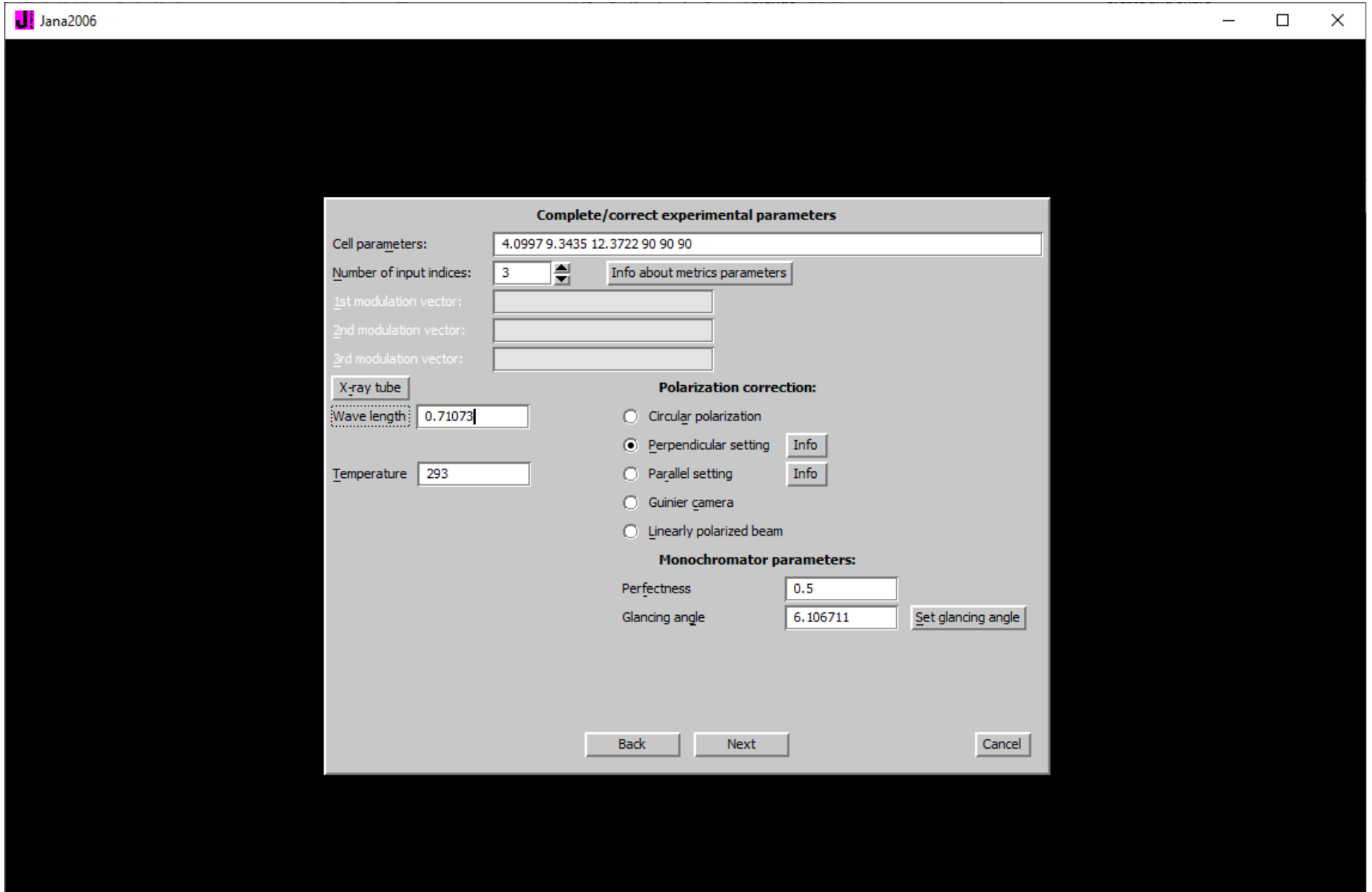
Select single crystal with known diffractometer formats



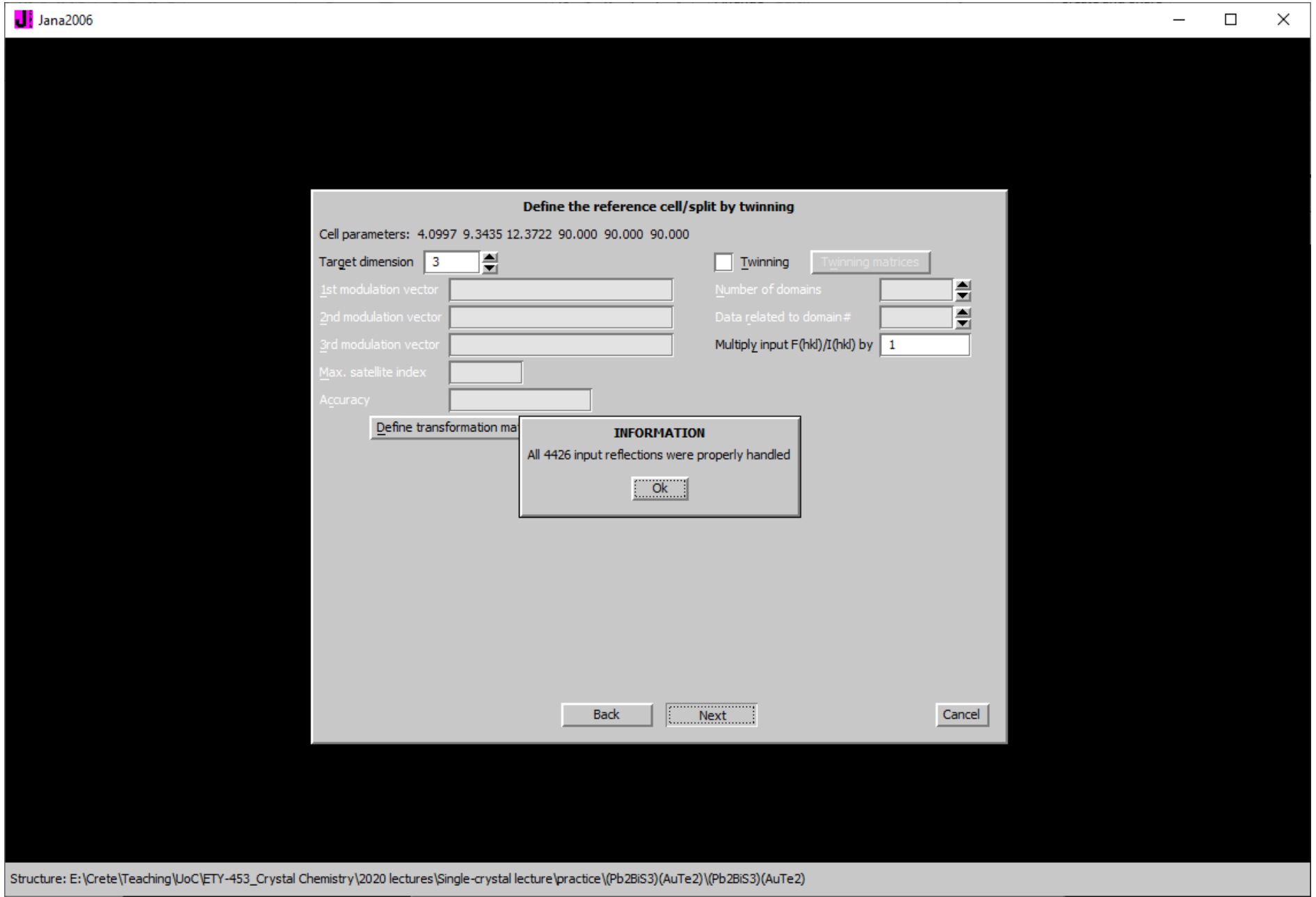
Select the appropriate instrument/format



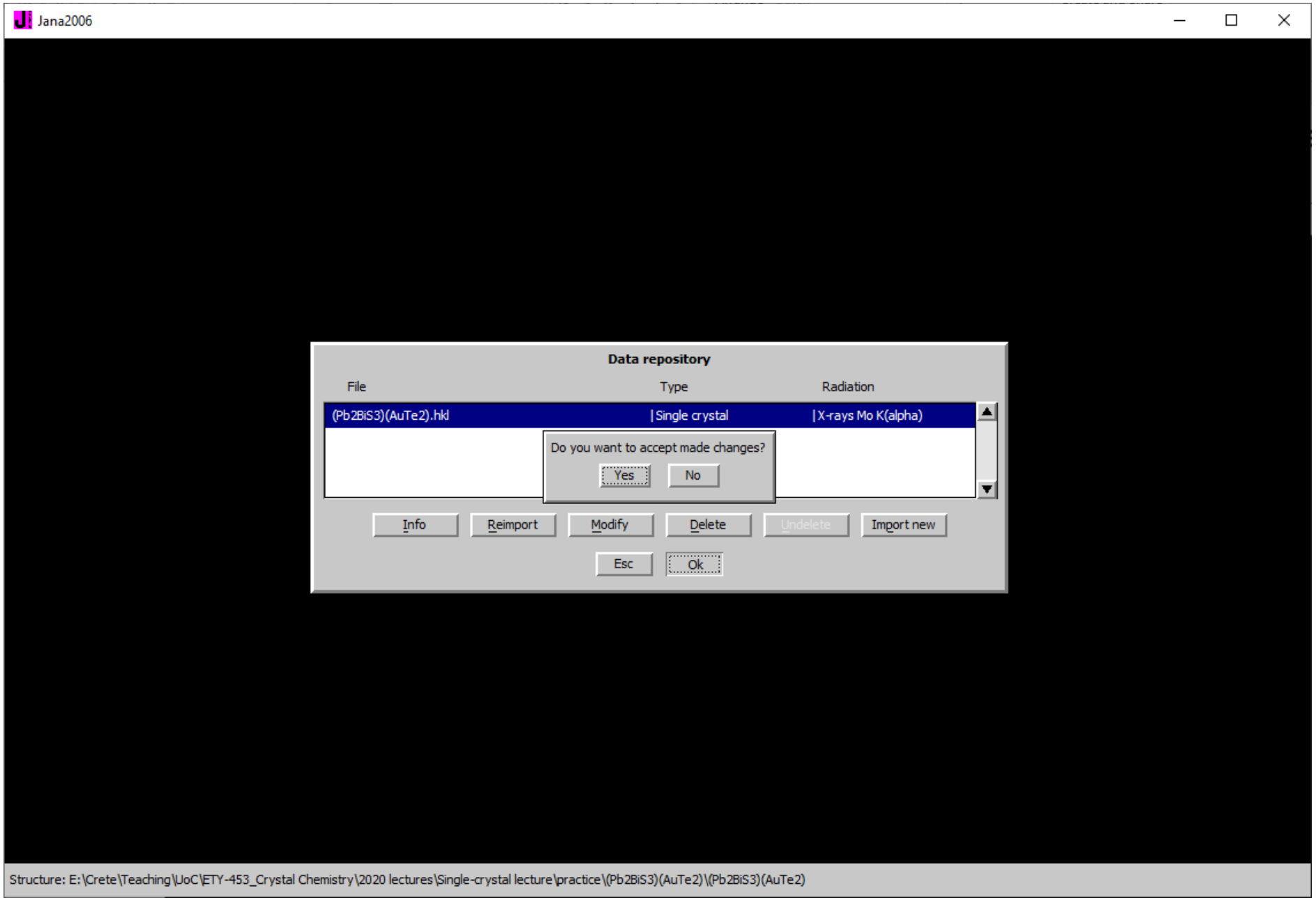
Check that your data are properly imported
Unit cell, wavelength and temperature should be as in the experiment



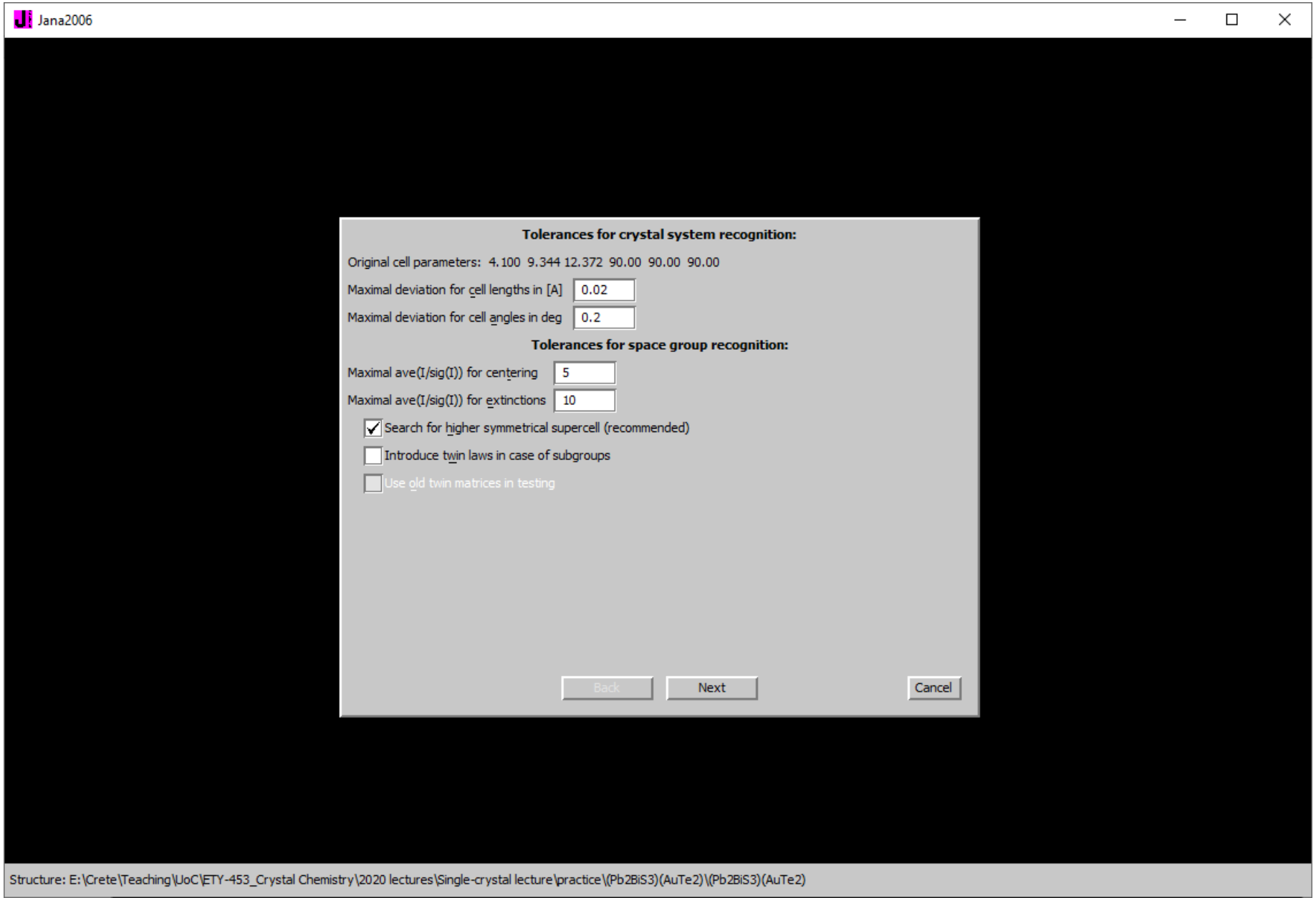
Import your reflection file (hkl) by clicking through to the menu below



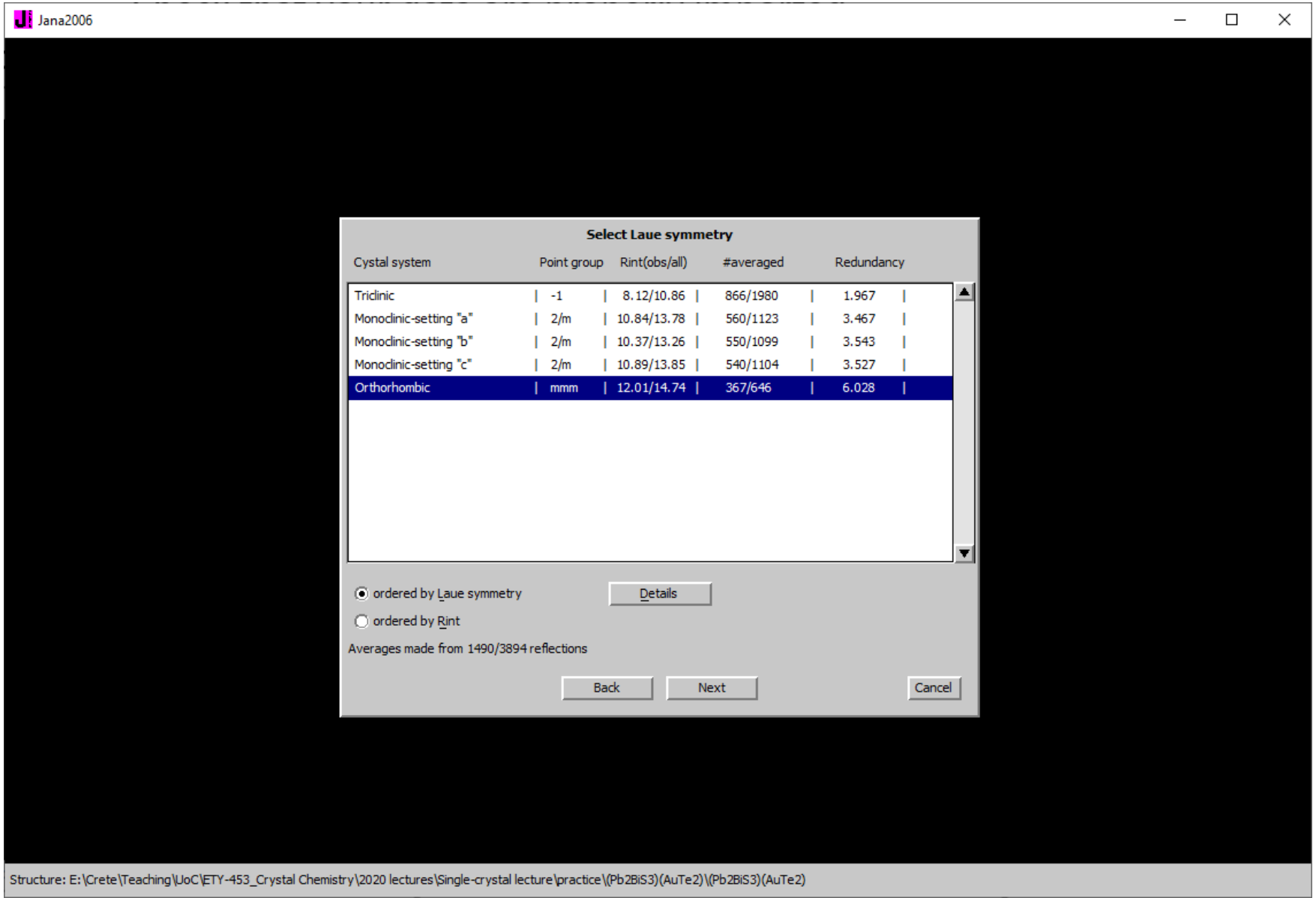
Click through and accept your hkl file, if correct



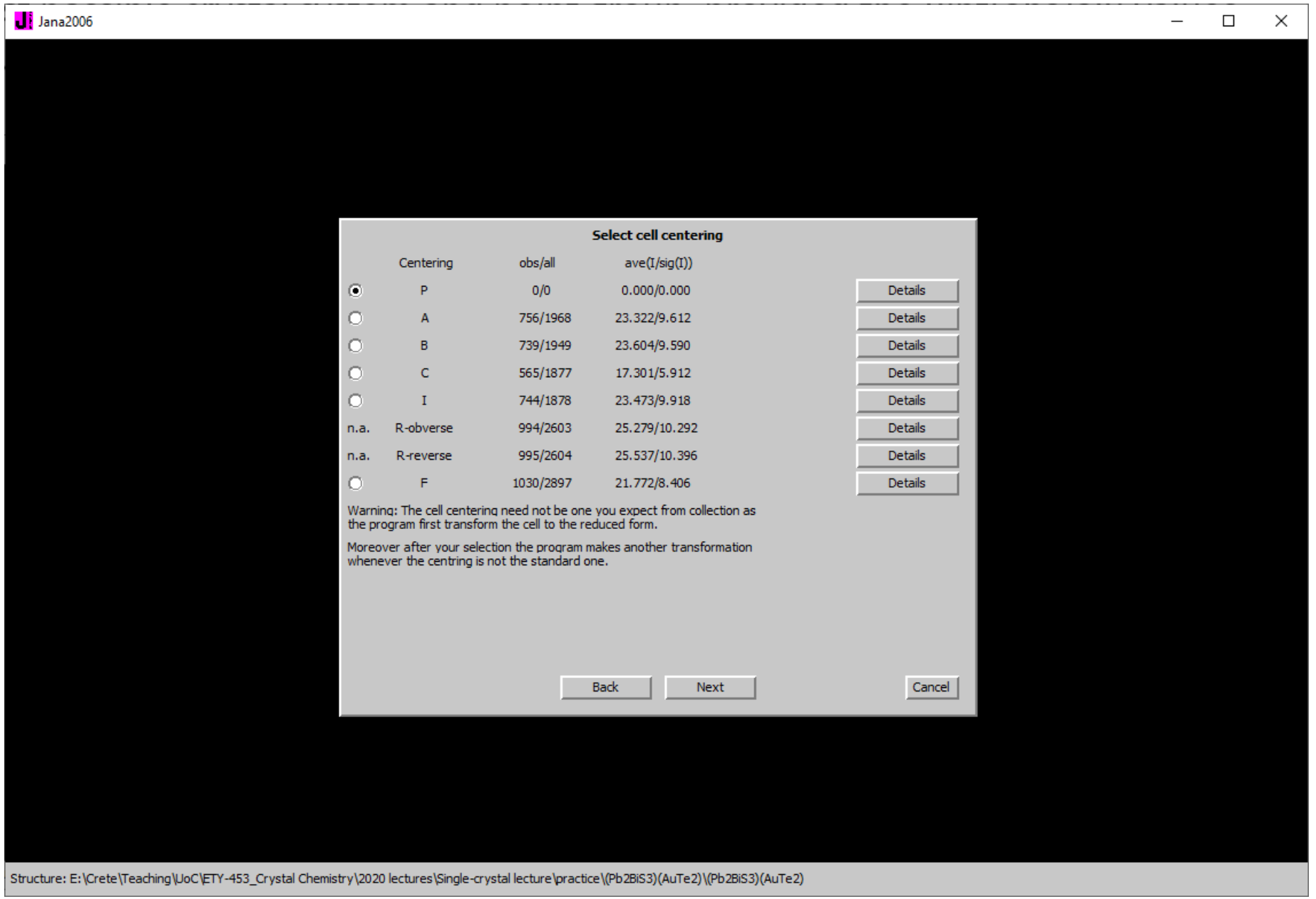
You are now in the process of finding your space group.
Keep default commands



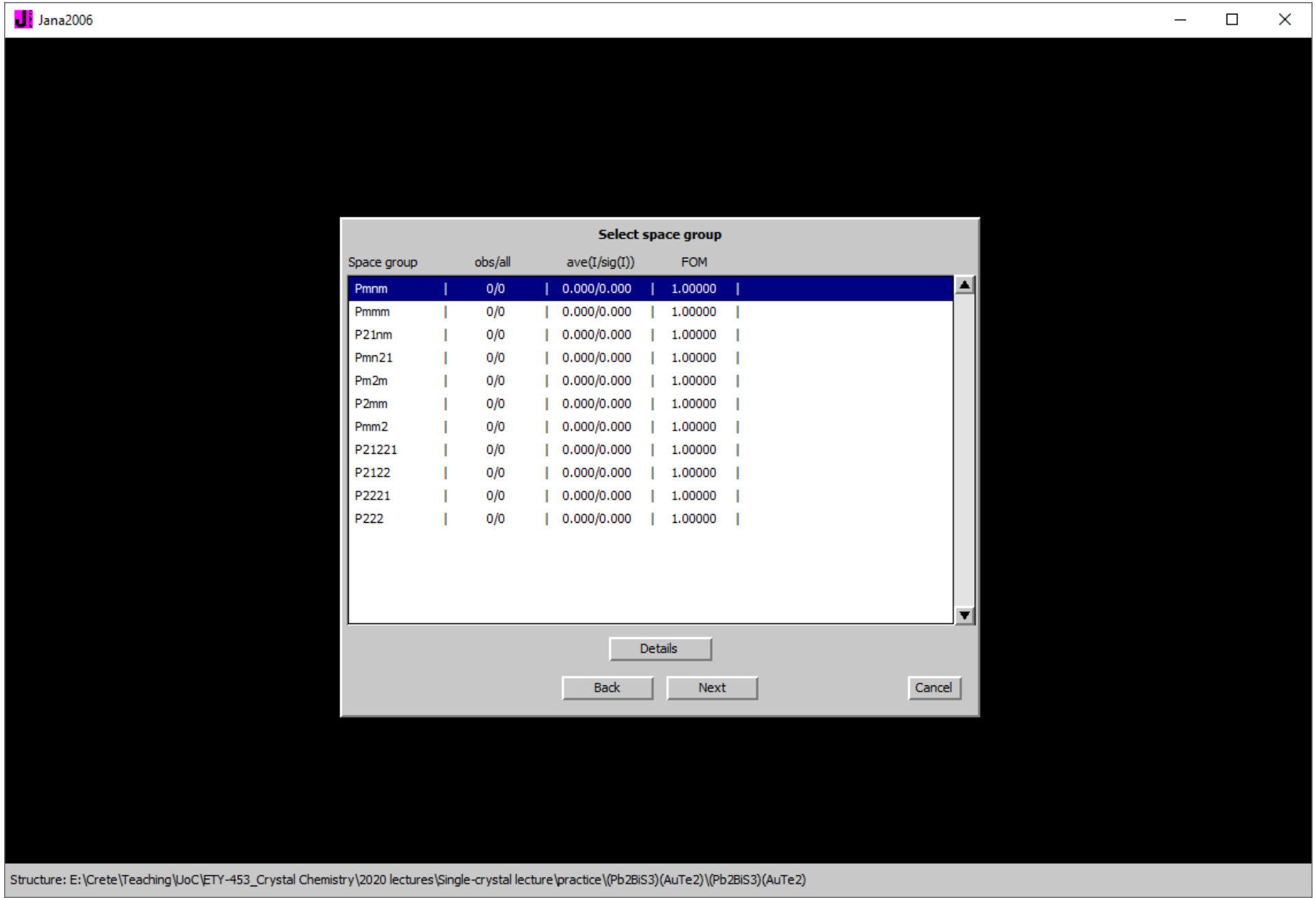
Select the highest possible crystal system and point group, provided the Rint(obs/all) values are comparable. Rint will always be highest for the highest symmetry, so this requires some experience. You can return here at any time and select a different one.



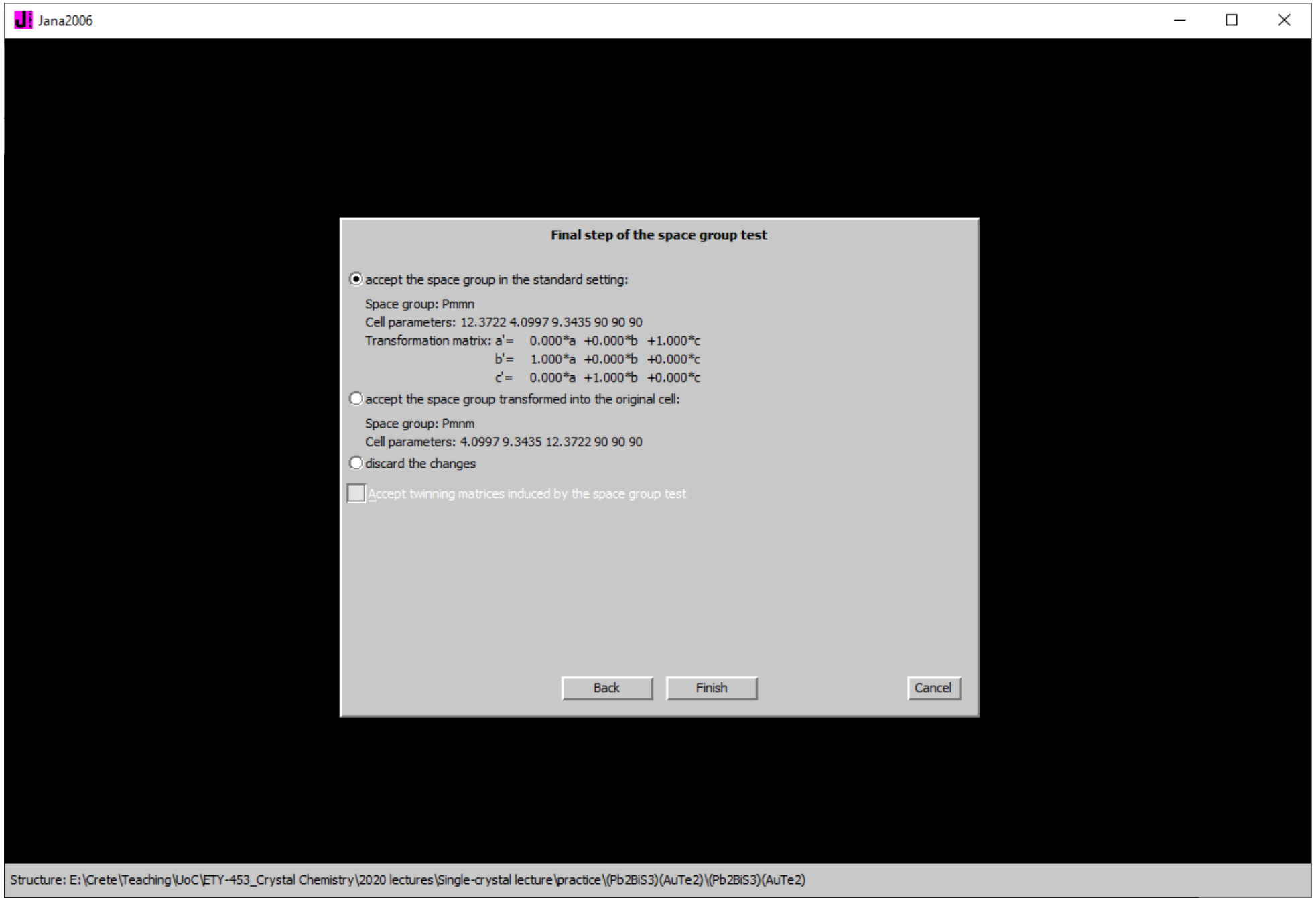
Find your unit cell centering. Look for the zeroes (no systematic absence violations) with the highest symmetry



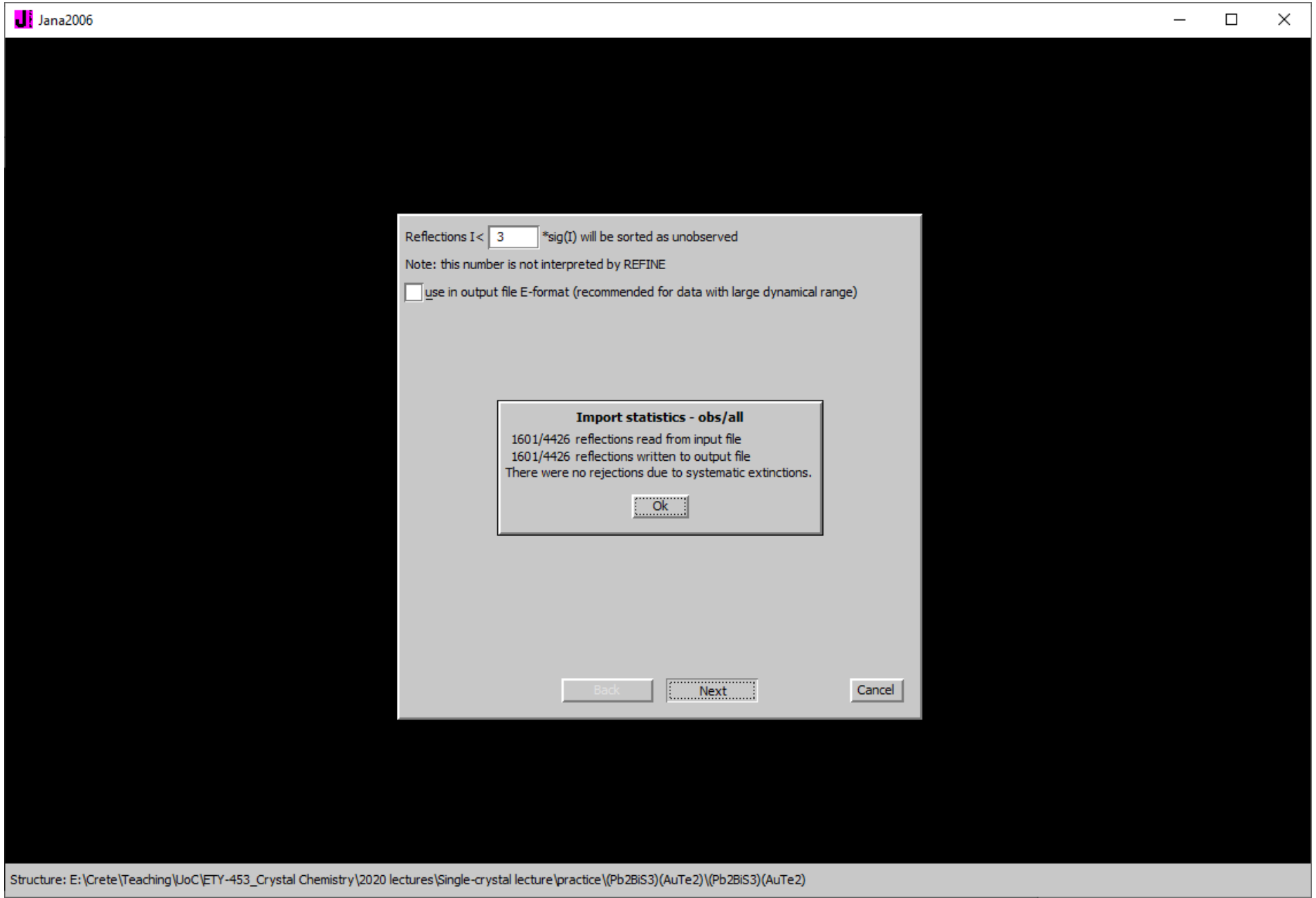
Select the space group with the highest possible symmetry



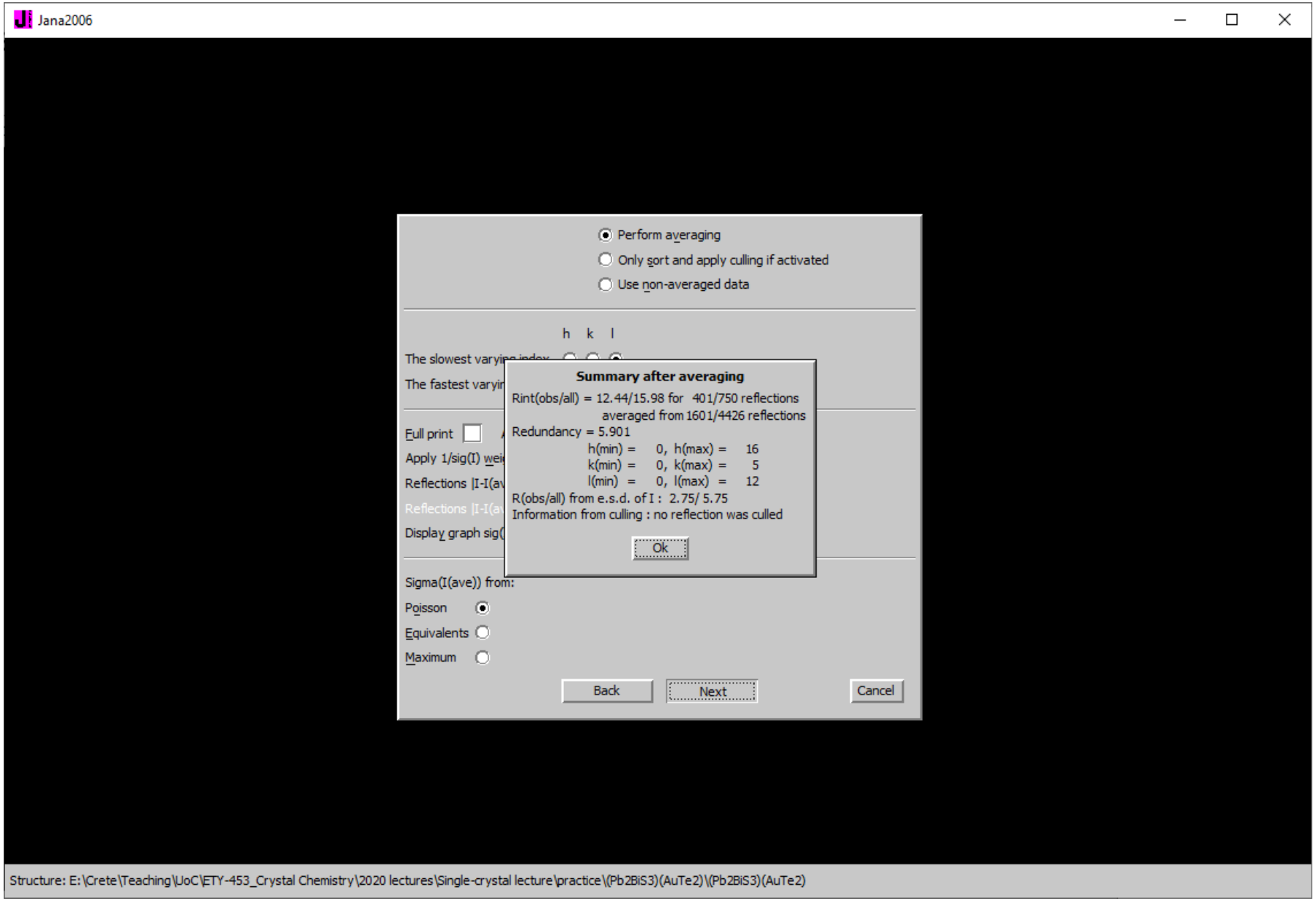
Accept you unit cell and proceed (standard or not is a matter of taste)



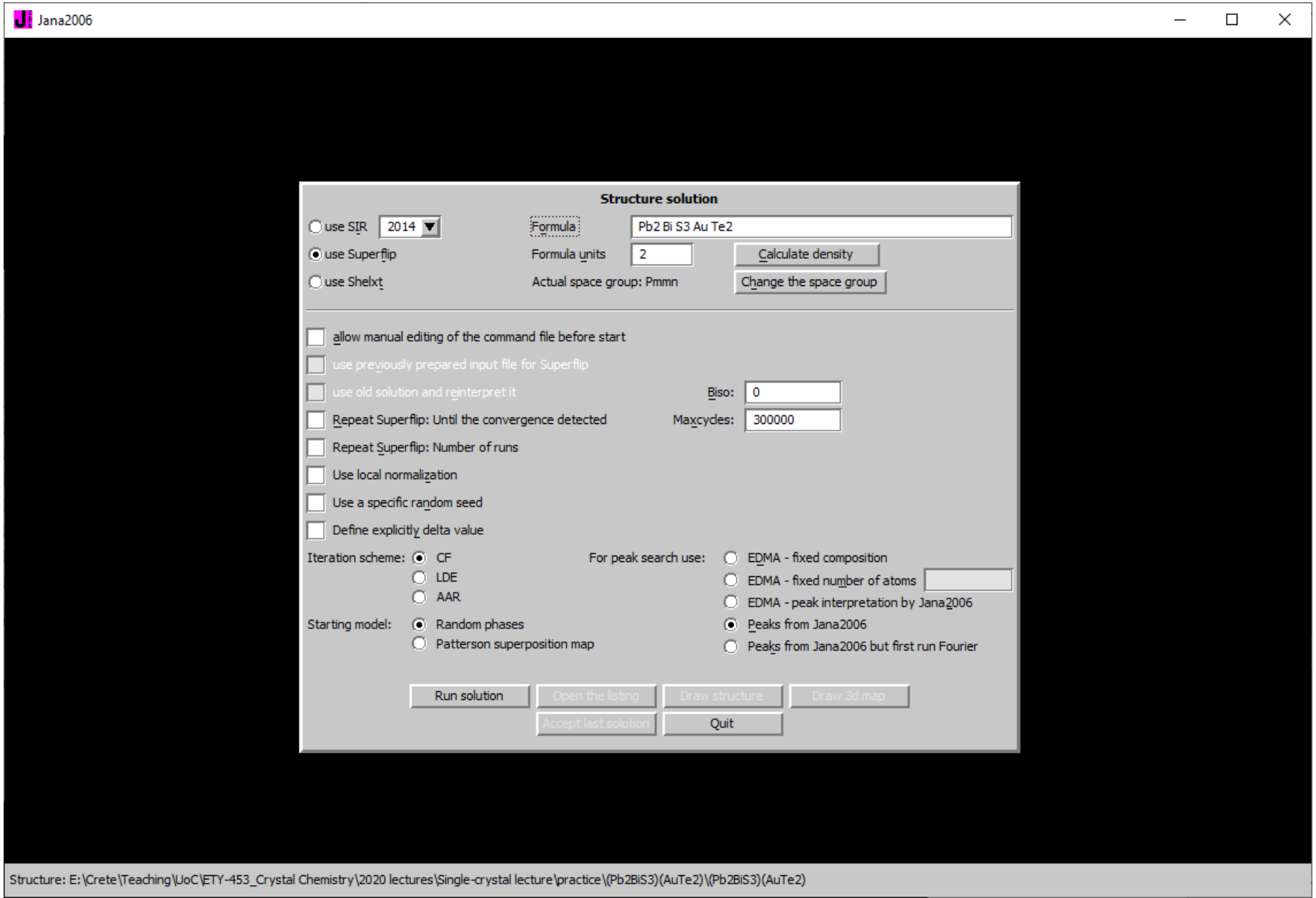
Read through the transformed hkl file. Keep default settings



Read and merge your (symmetry equivalent) reflections. Keep default settings. Accept and proceed.



This is where you solve the structure. Type your formula and number of formula units as your best estimate. All elements present should be typed. Check density to make sense.



Make sure

- Superflip

(the program),

- CF (the method)
- random phases

(the starting model)

are selected.

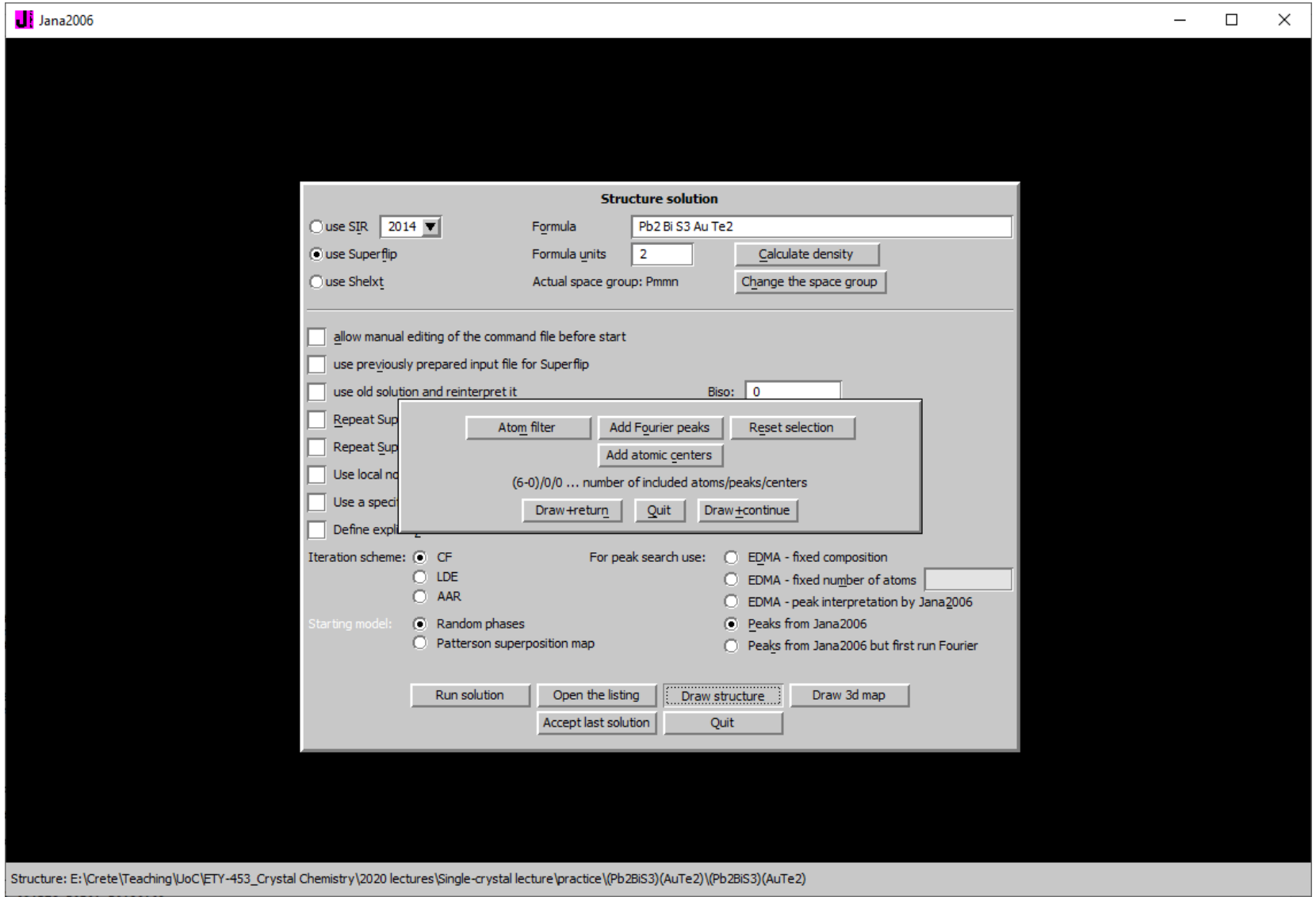
Run solution

Jana2006

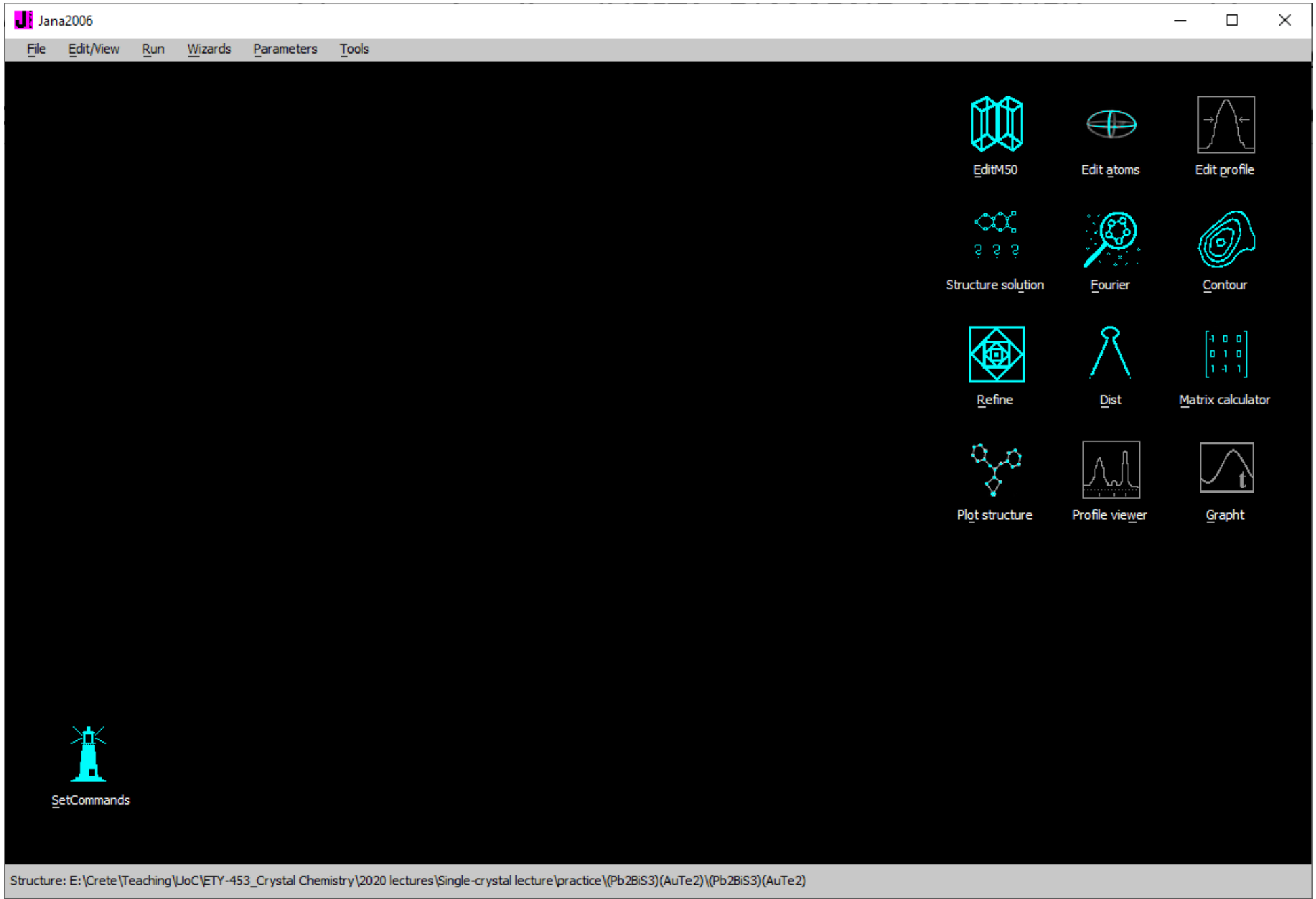
Find | Find next | Go to | Print | PgTop | Open in editor | Close

```
              -1:           -x1           -x2           -x3    6.528    XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
        a(0,0,1):        1/2+x1            x2           -x3   49.305    XXXXXXXXXXXXXXXXXXXXXXXXXX
        b(0,0,1):            x1       1/2+x2           -x3   57.411    XXXXXXXXXXXXXXXXXXXXXX
        2(0,1,0):           -x1            x2           -x3   77.564    XXXXXXXXXXX
        2(1,0,0):            x1           -x2           -x3   77.735    XXXXXXXXXXX
        b(1,0,0):           -x1       1/2+x2            x3   77.912    XXXXXXXXXXX
        a(0,1,0):        1/2+x1           -x2            x3   79.292    XXXXXXXXXX
        m(0,0,1):            x1            x2           -x3   82.672    XXXXXXXXX
        n(1,0,0):           -x1       1/2+x2       1/2+x3  136.028    X
      2_1(0,0,1):           -x1           -x2       1/2+x3  139.358    X
        c(1,0,0):           -x1            x2       1/2+x3  142.148    X
        n(0,1,0):        1/2+x1           -x2       1/2+x3  148.203    X
        c(0,1,0):            x1           -x2       1/2+x3  149.080    X

-------------------------------------------------
Space group derived from the symmetry operations:
-------------------------------------------------
    HM symbol:      Pmmn
    Hall symbol:    -P 2ab 2a
    Fingerprint:    3300320n{641Y63}20 (1/4,3/4,0)
    Symmetry operations:
              1:            x1            x2            x3
        2(0,0,1):        1/2-x1        1/2-x2            x3
      2_1(1,0,0):        1/2+x1           -x2           -x3
             -1:           -x1           -x2           -x3
      2_1(0,1,0):           -x1        1/2+x2           -x3
        n(0,0,1):        1/2+x1        1/2+x2           -x3
        m(1,0,0):        1/2-x1            x2            x3
        m(0,1,0):            x1        1/2-x2            x3


###############################################
# Search for the origin of the space group #
###############################################


Position of the origin in the CF map:
  0.6208  0.9422  0.9742
Agreement factors of individual generators:
Number smb agreement
   6   n        0.20
   7   m        0.32
   8   m        6.00

Overall agreement factor:   3.73

You can obtain more information about the reconstructed reflection phases by using 'expandedlog yes'.

Electron density written to file (Pb2BiS3)(AuTe2)_Superflip.m81.


-----------------------------------------------
End of the calculation: 09.DEC 2020, 22:18:35
-----------------------------------------------
Superflip version: 05/17/16 12:53
```

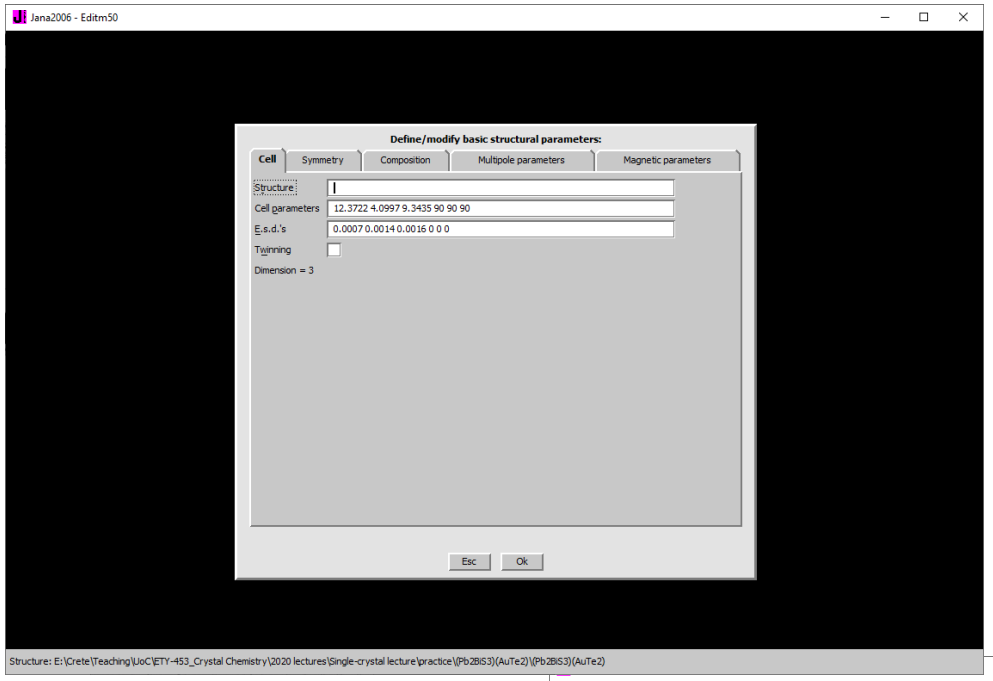
Draw your structure with your visualizer (VESTA, DIAMOND, MERCURY or anything else) to make sure you are happy (Draw + return). You need to set the software path in JANA2006 (Tools-> Programs-> . Accept solution if you are happy with it, else try a different model.

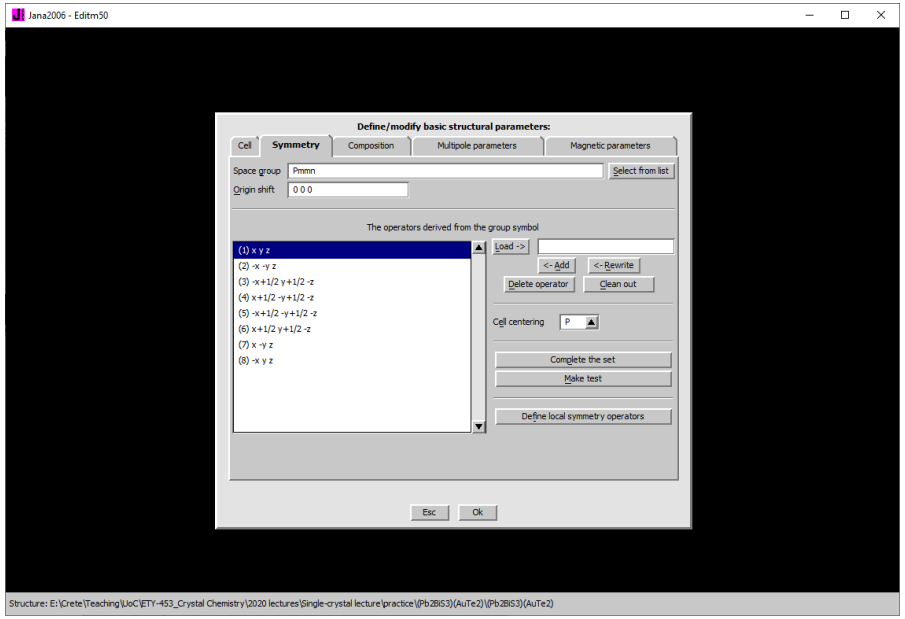


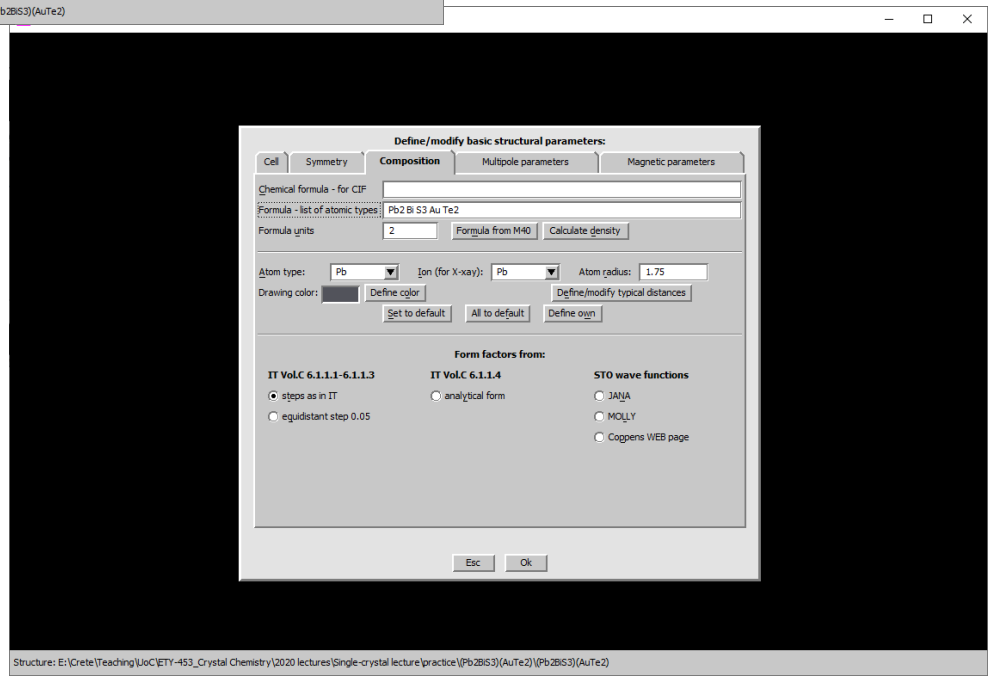
Inspect the tabs to make sure everything is correct



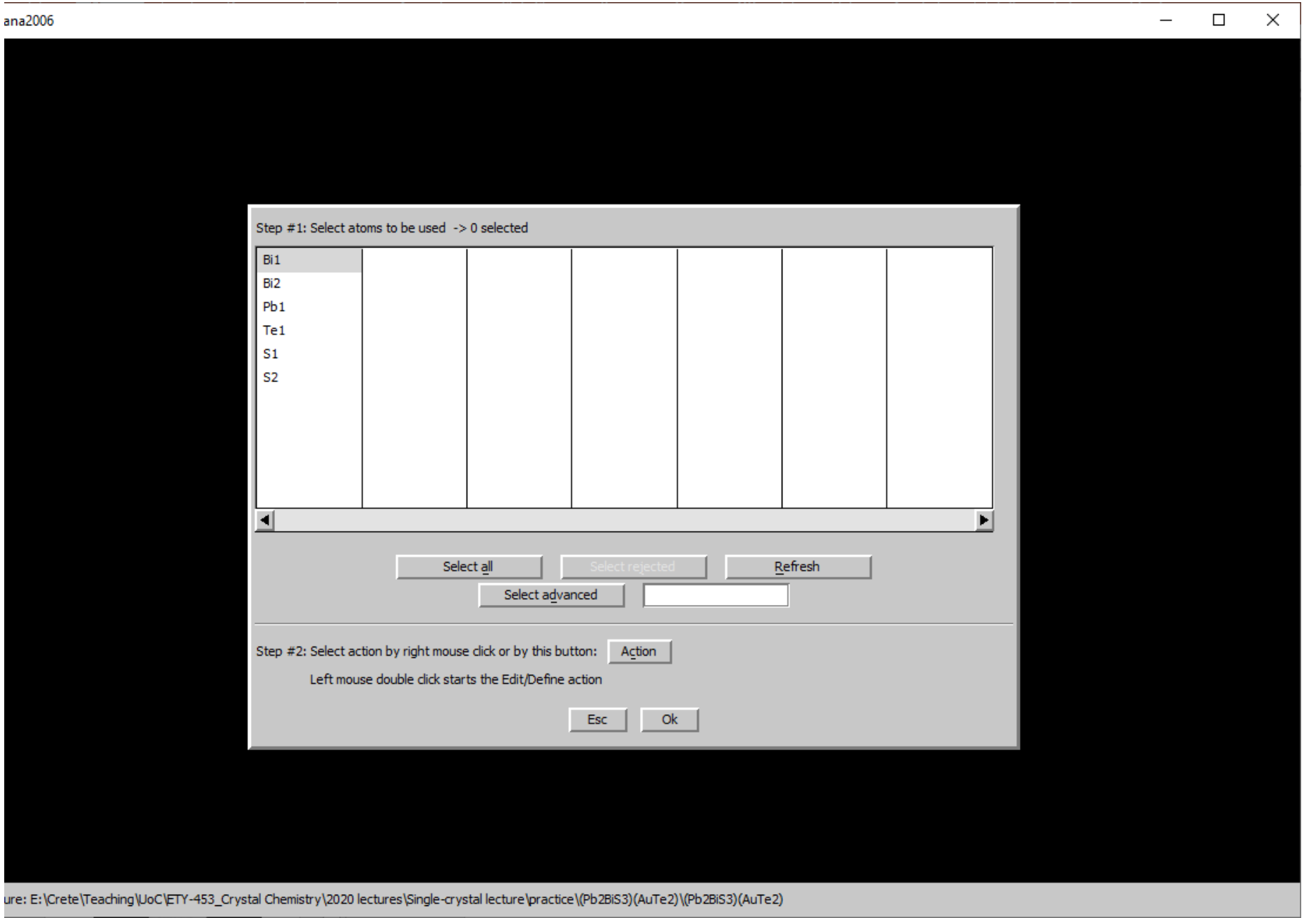
Check M50. The information should agree with your input



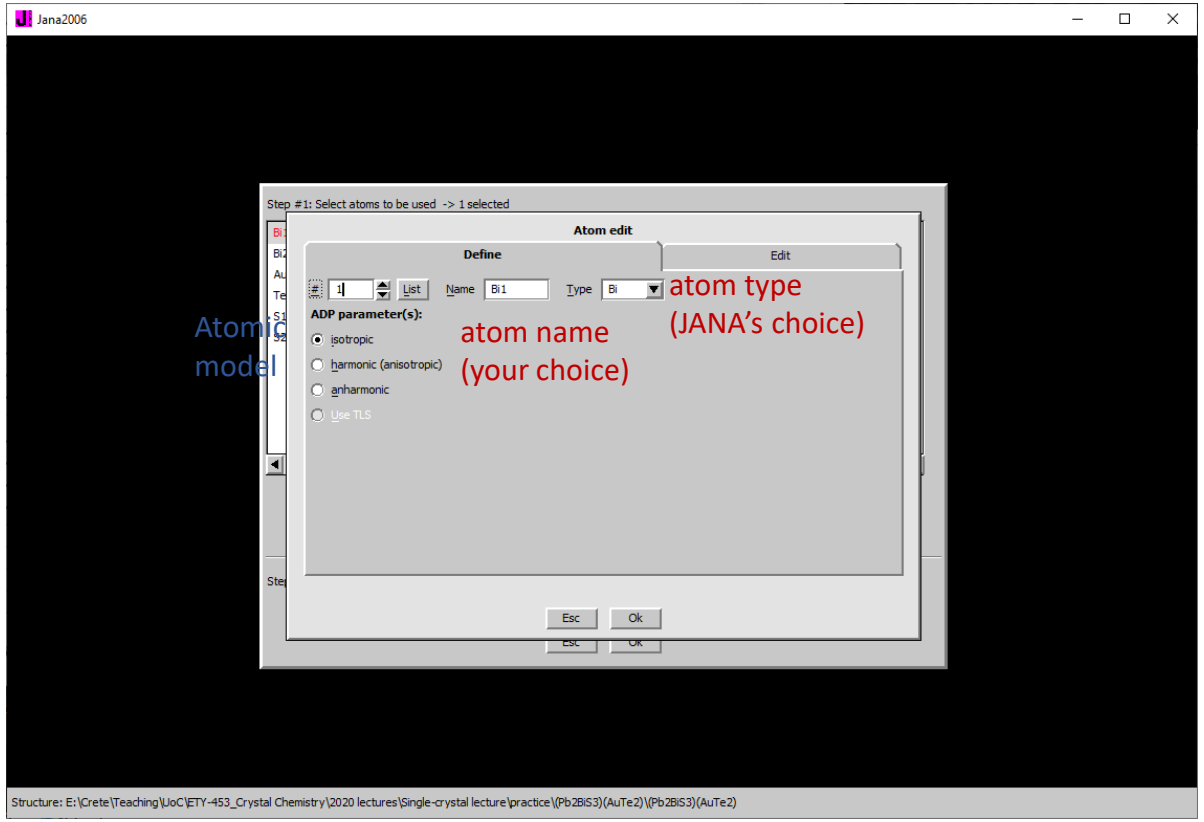


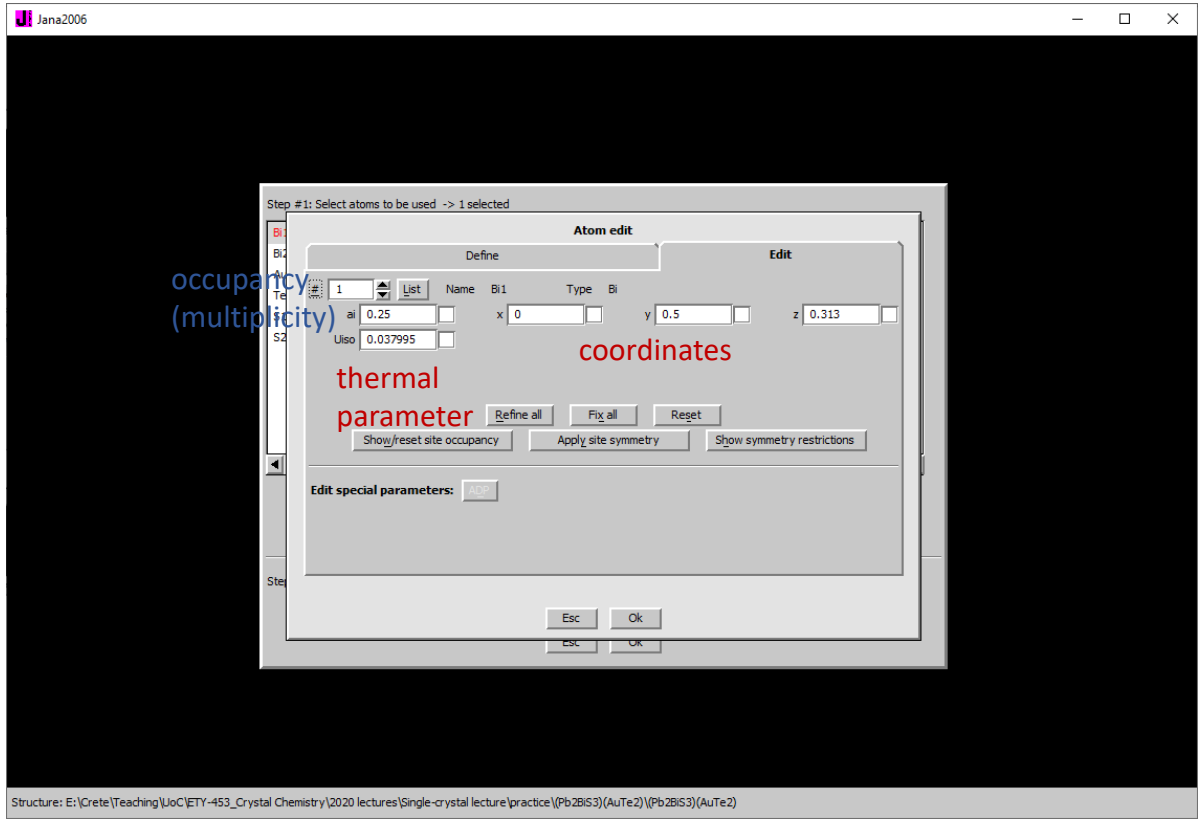


Check Edit atoms. This is what results from structure solution.

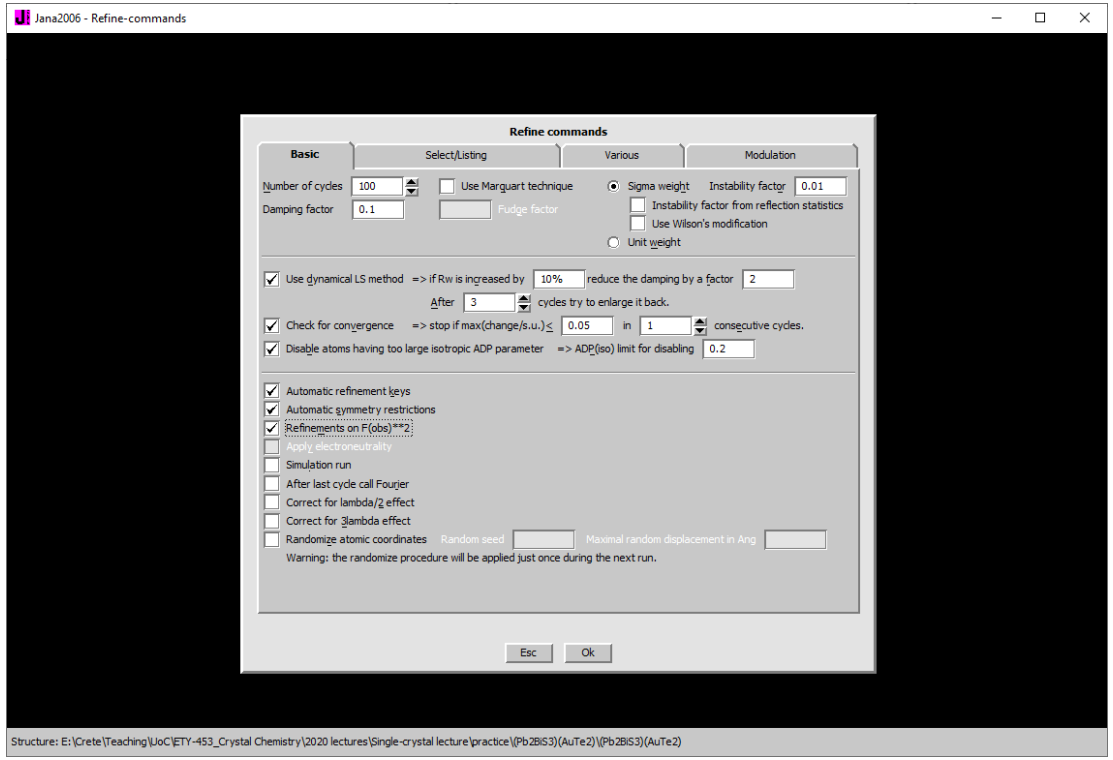


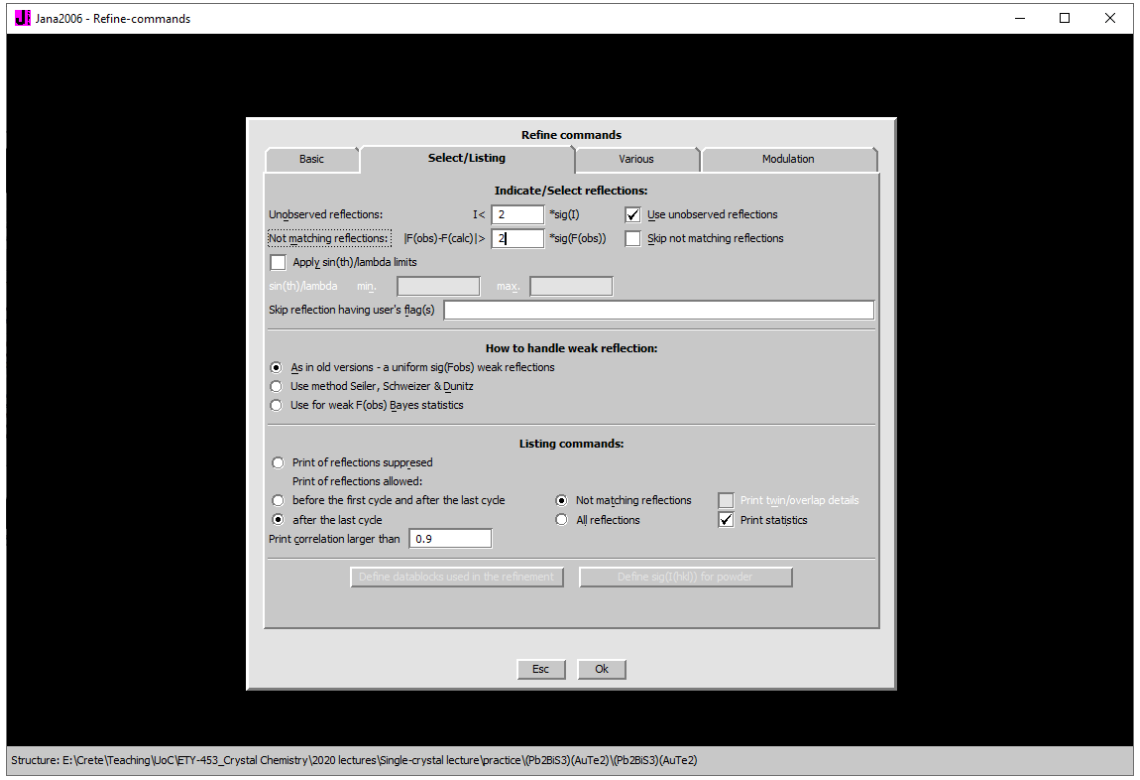
Inspect your atoms (double click)



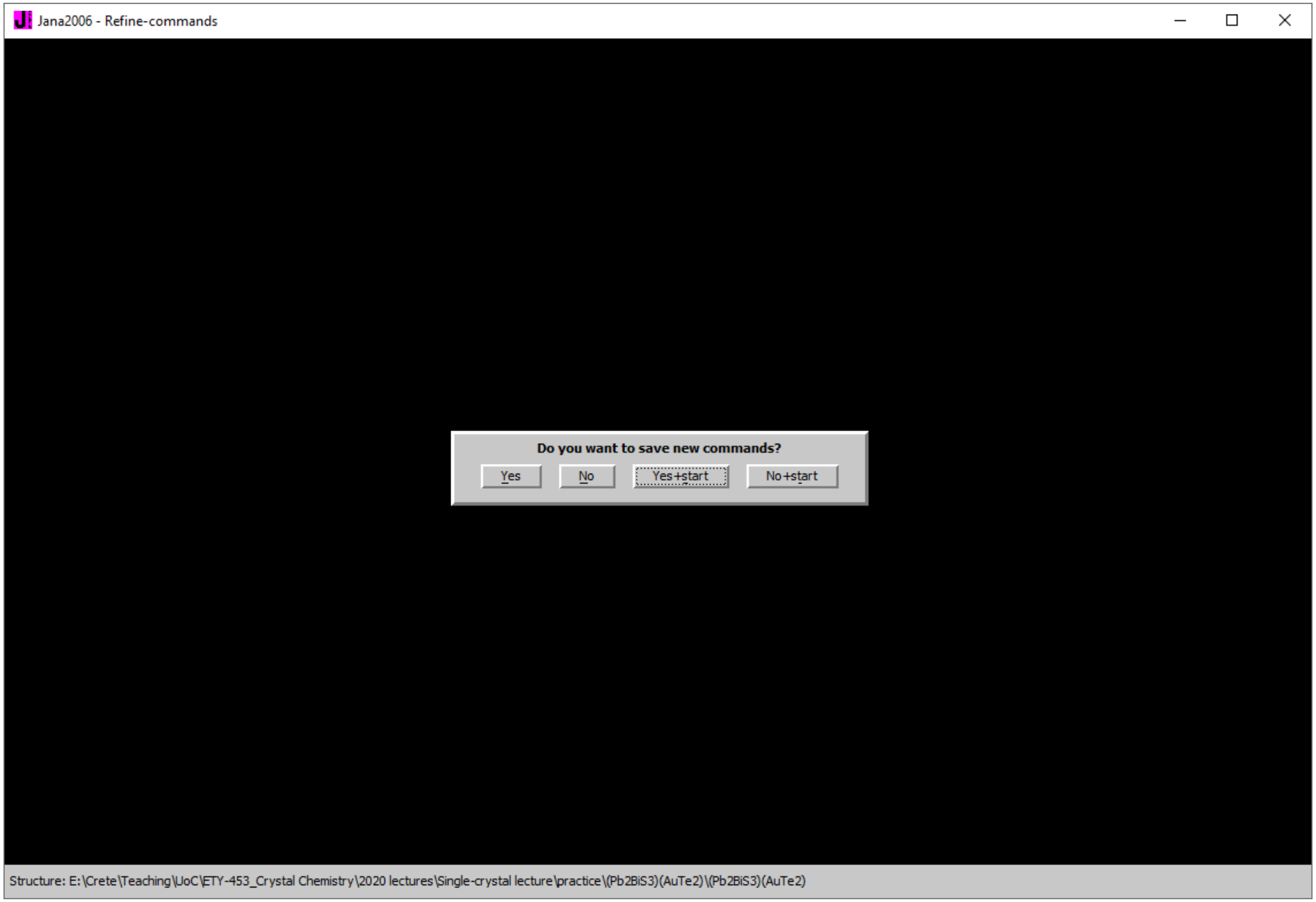


Setup the refinement process (right click)





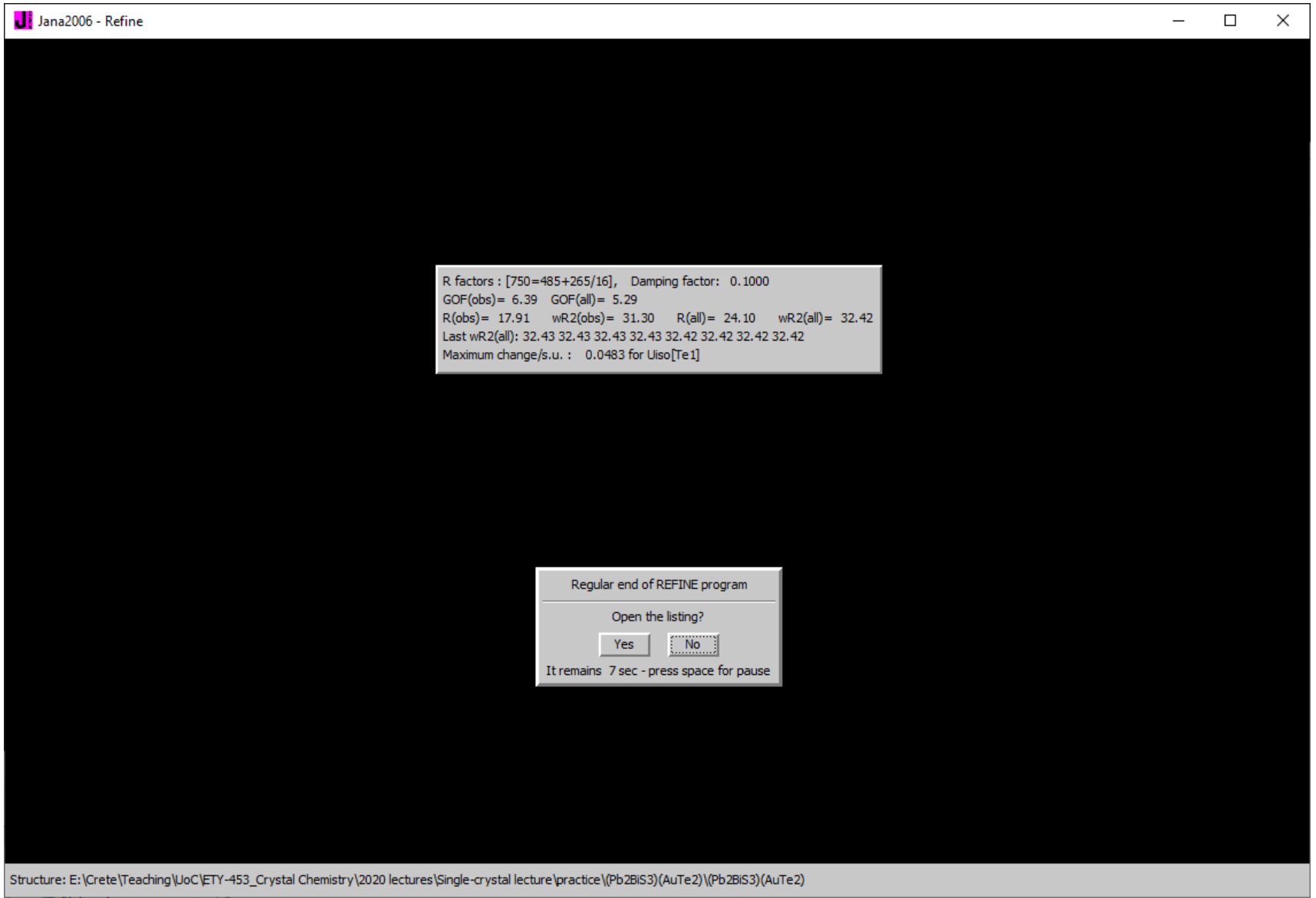
All set (Save and Start)



This is the result. GOF should be close to 1.

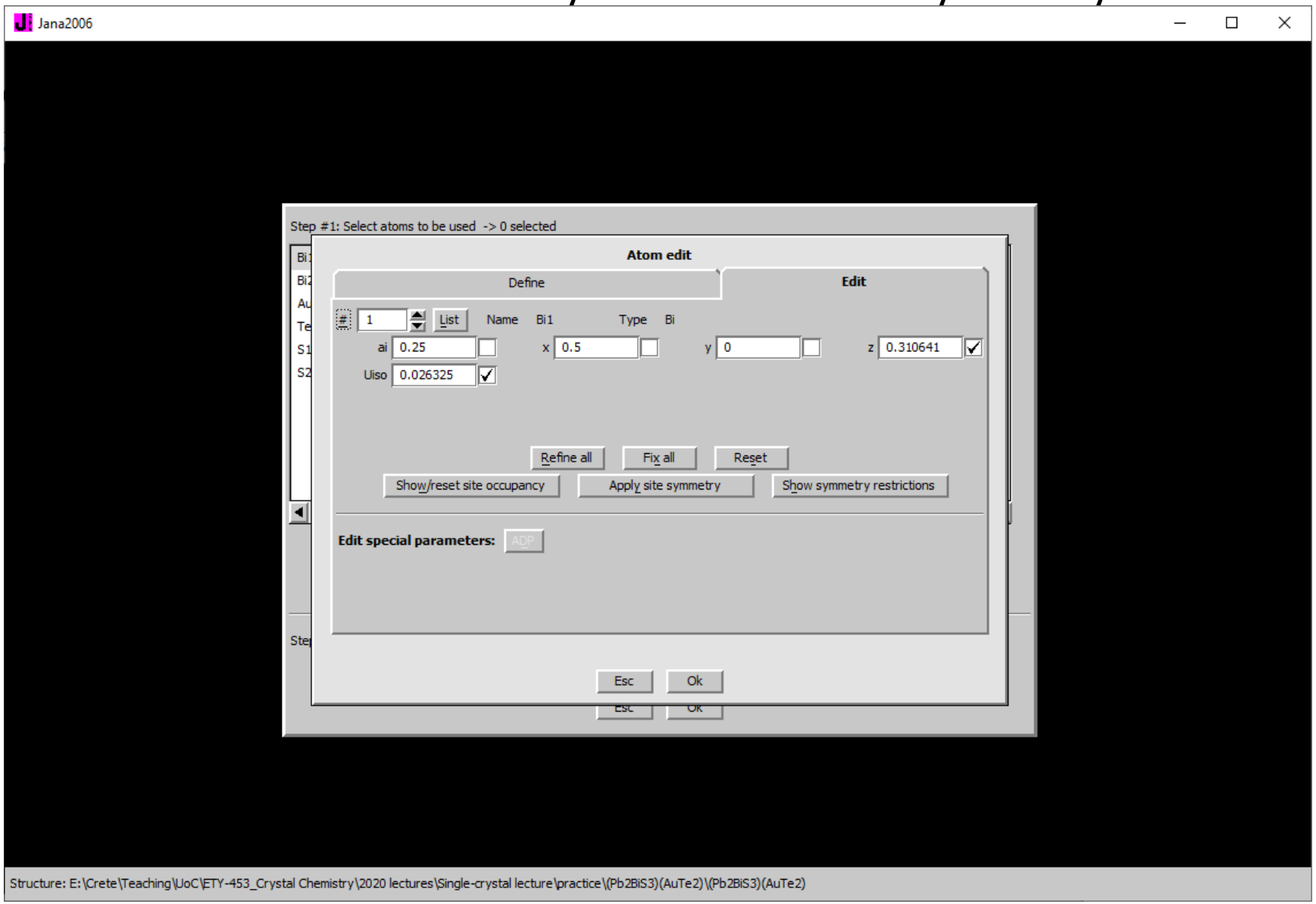
R(obs) (structure quality) should be as low as possible < 10%

Refinement stops once Maximum change < 0.05 or when cycles run out

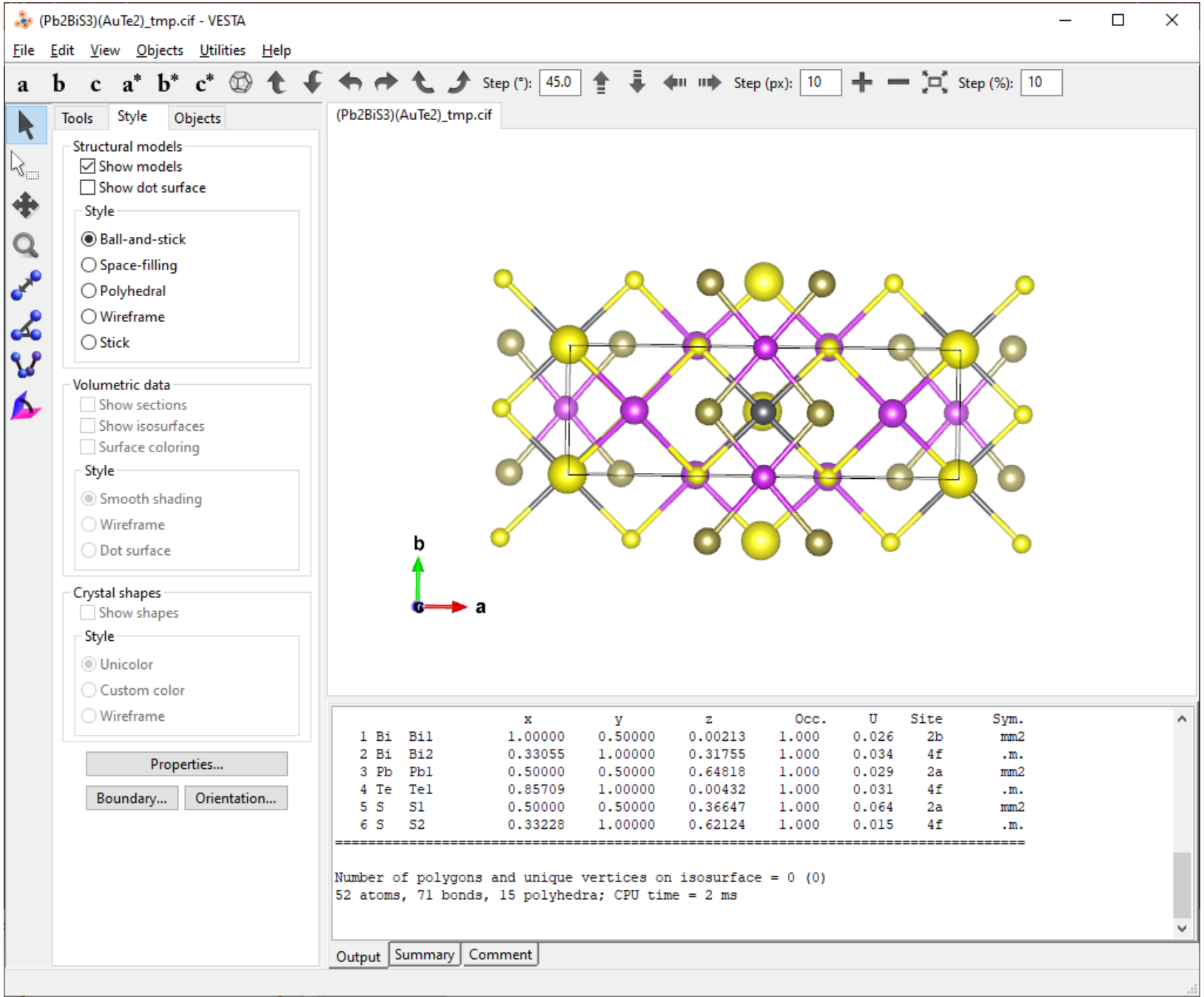


Inspect your atoms again

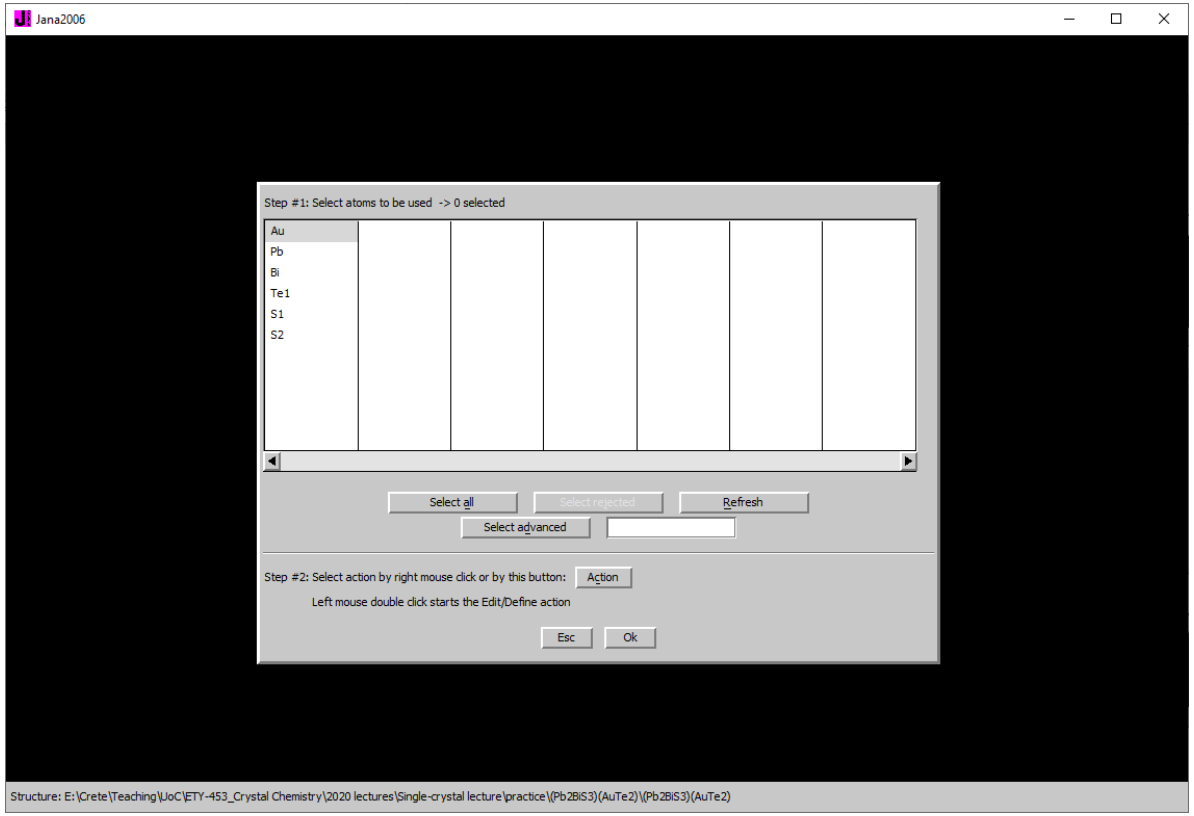
Thermal parameters and some coordinates do refine. Coordinates at special lattice positions do not refine. They are fixed due to symmetry

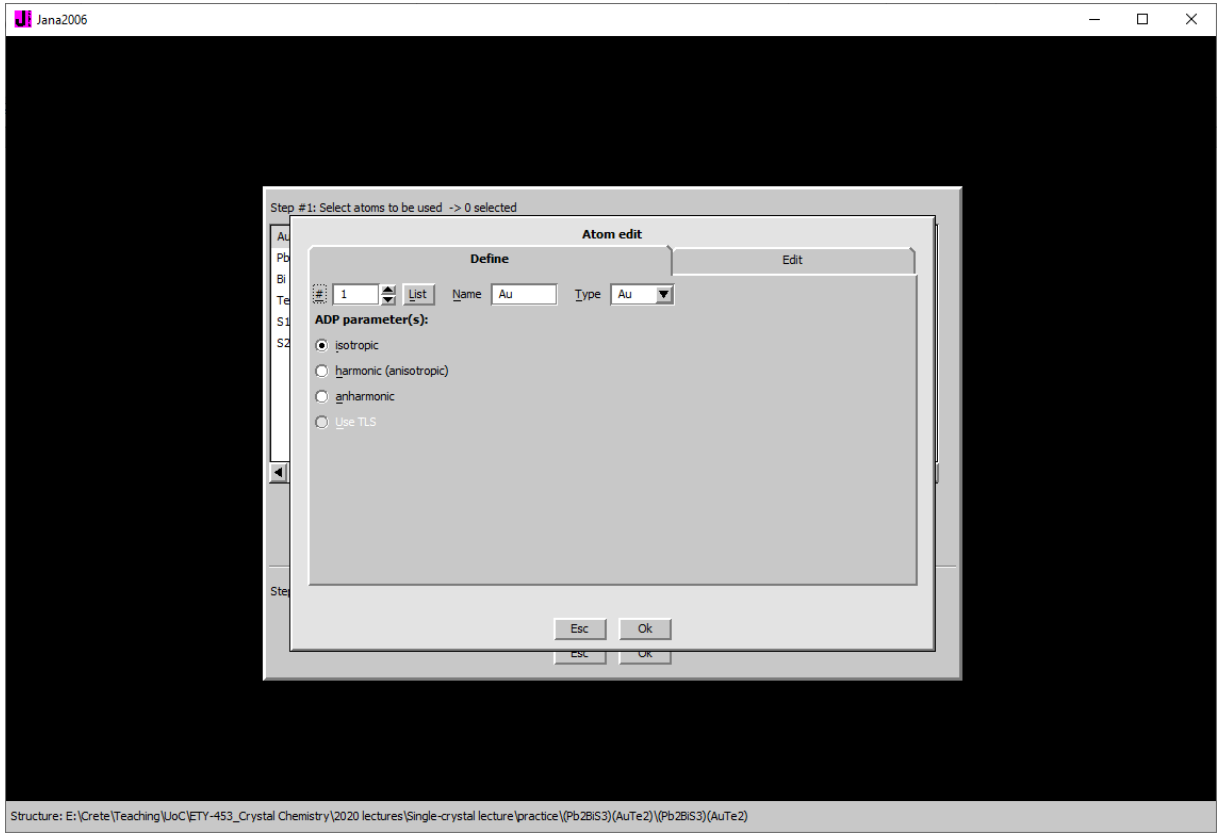


This is your structure so far. Some atoms look ok, but some atoms are mislabeled

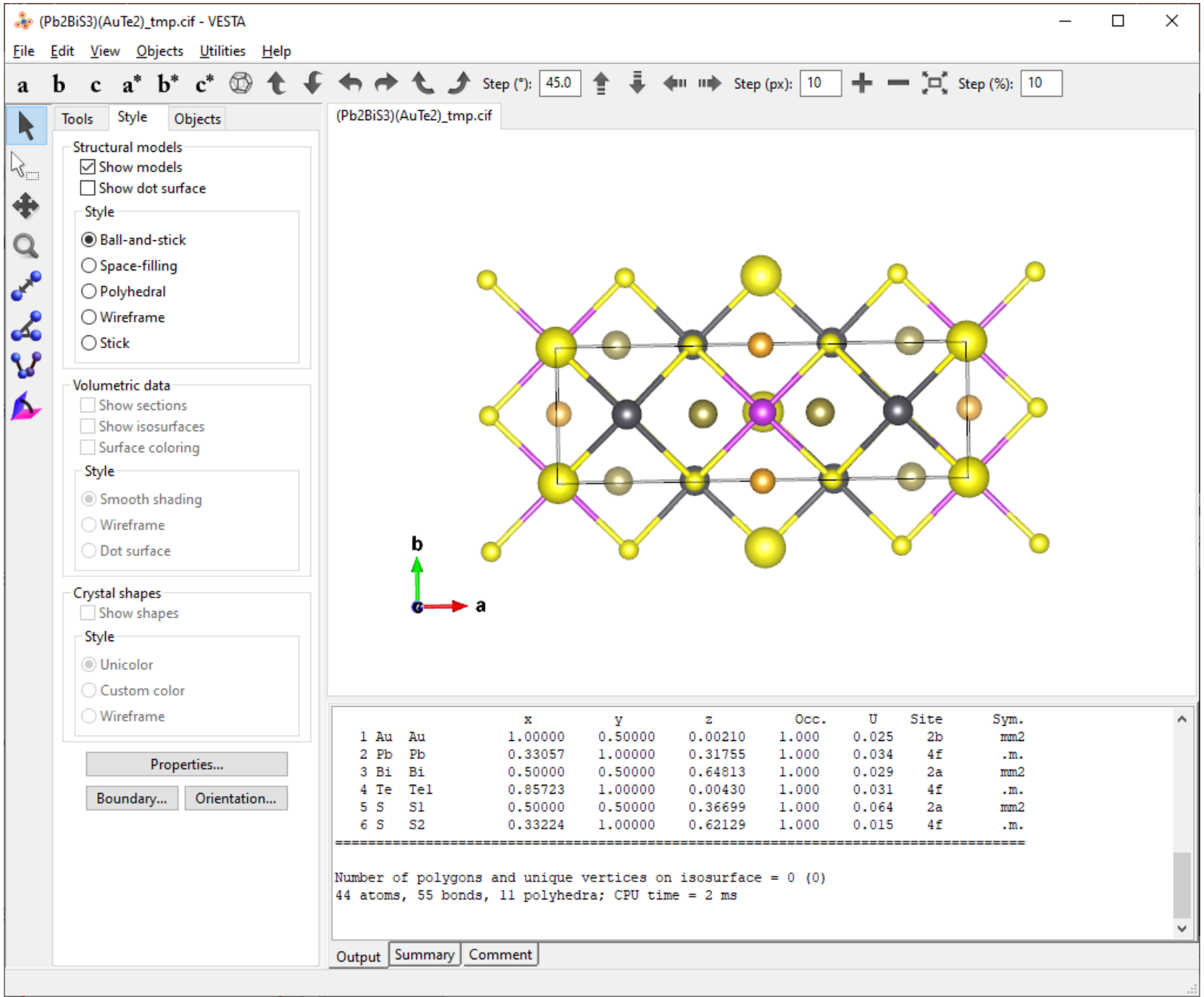


Change the atoms in a way it seems appropriate.

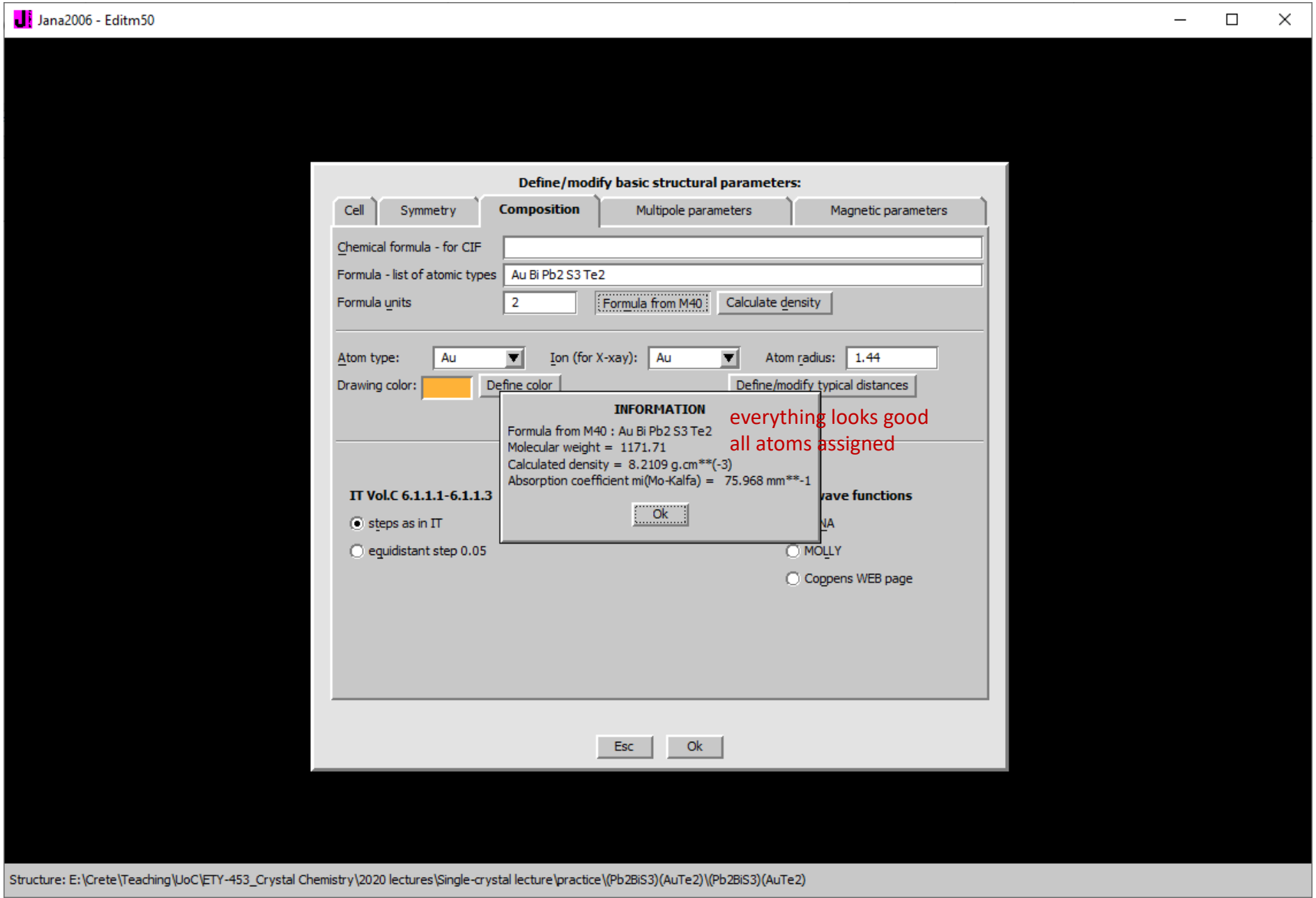




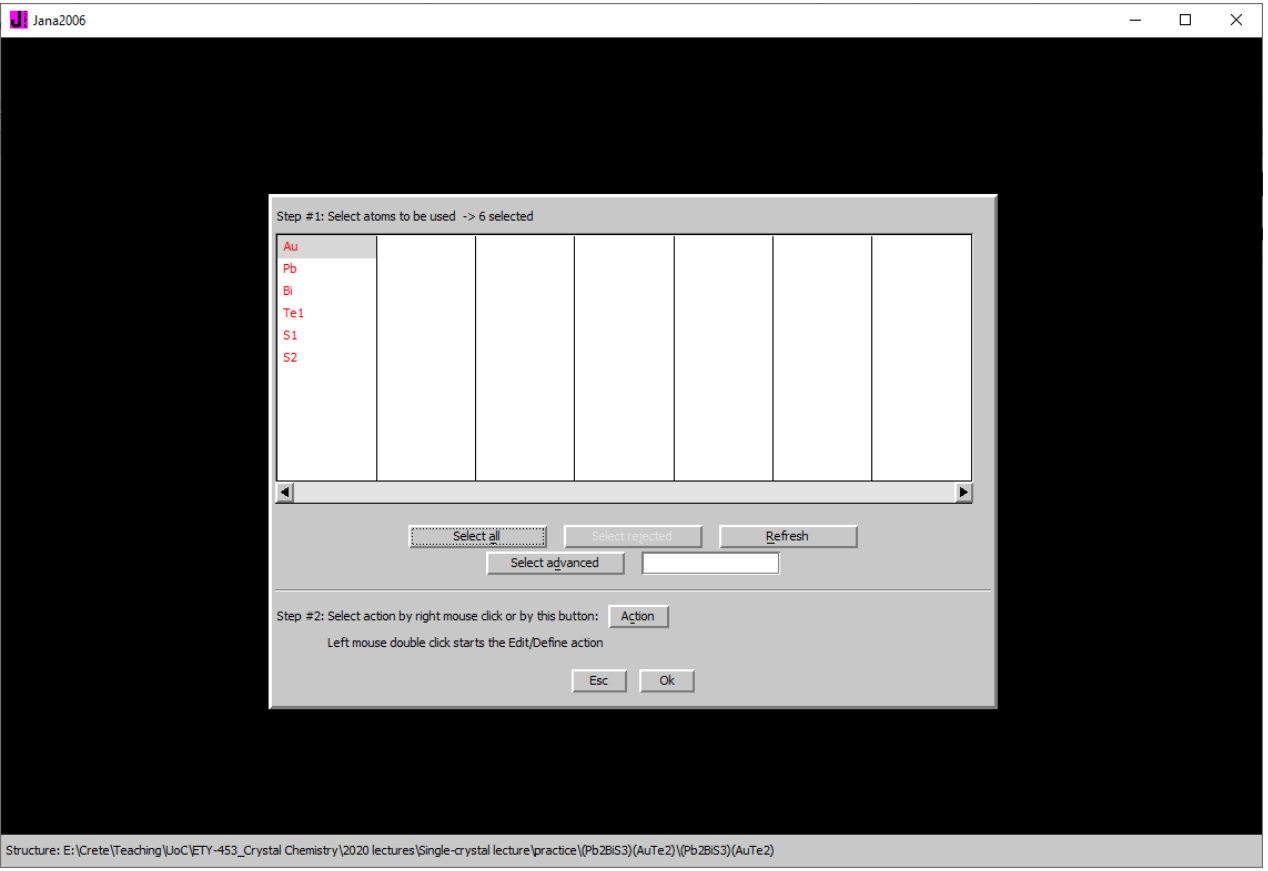
Refine again. This is the new structure

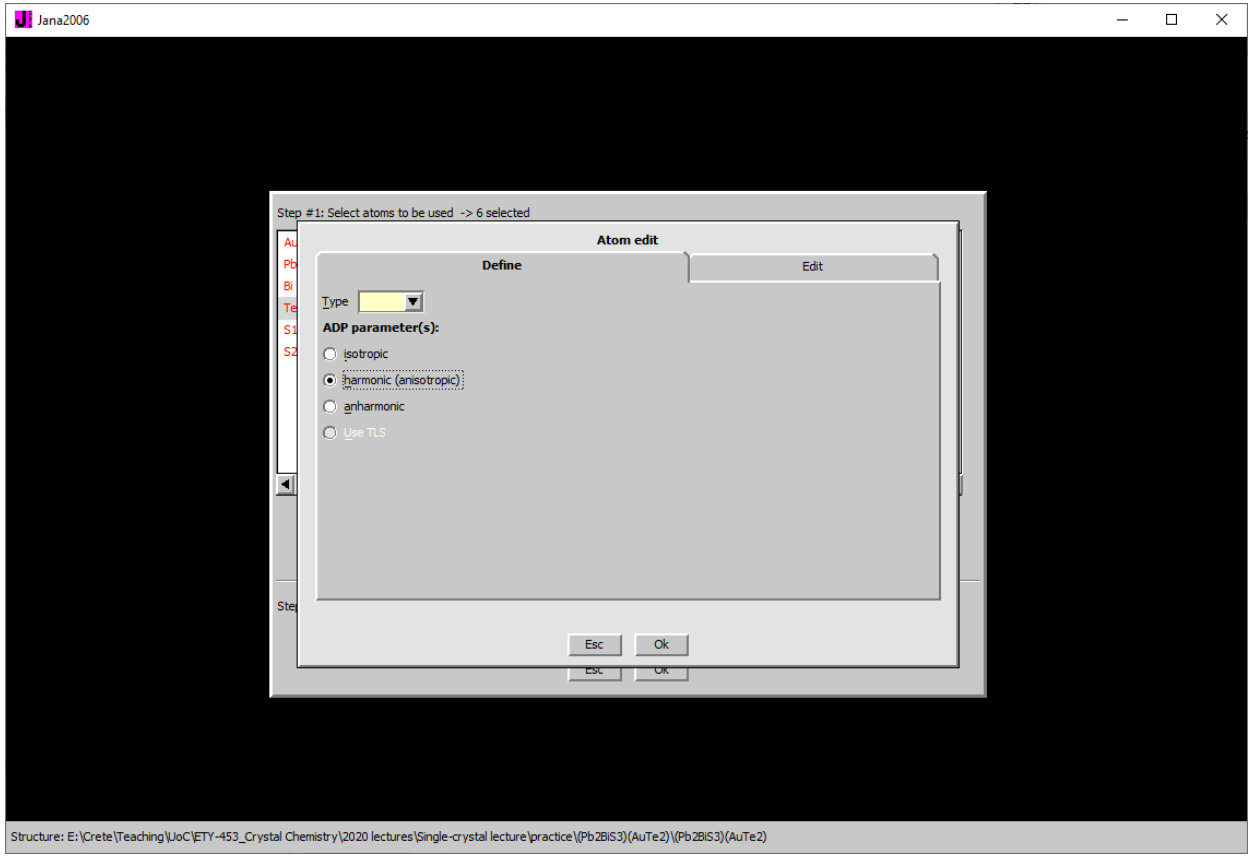


Check the formula in M50. Is the unit cell contents complete?

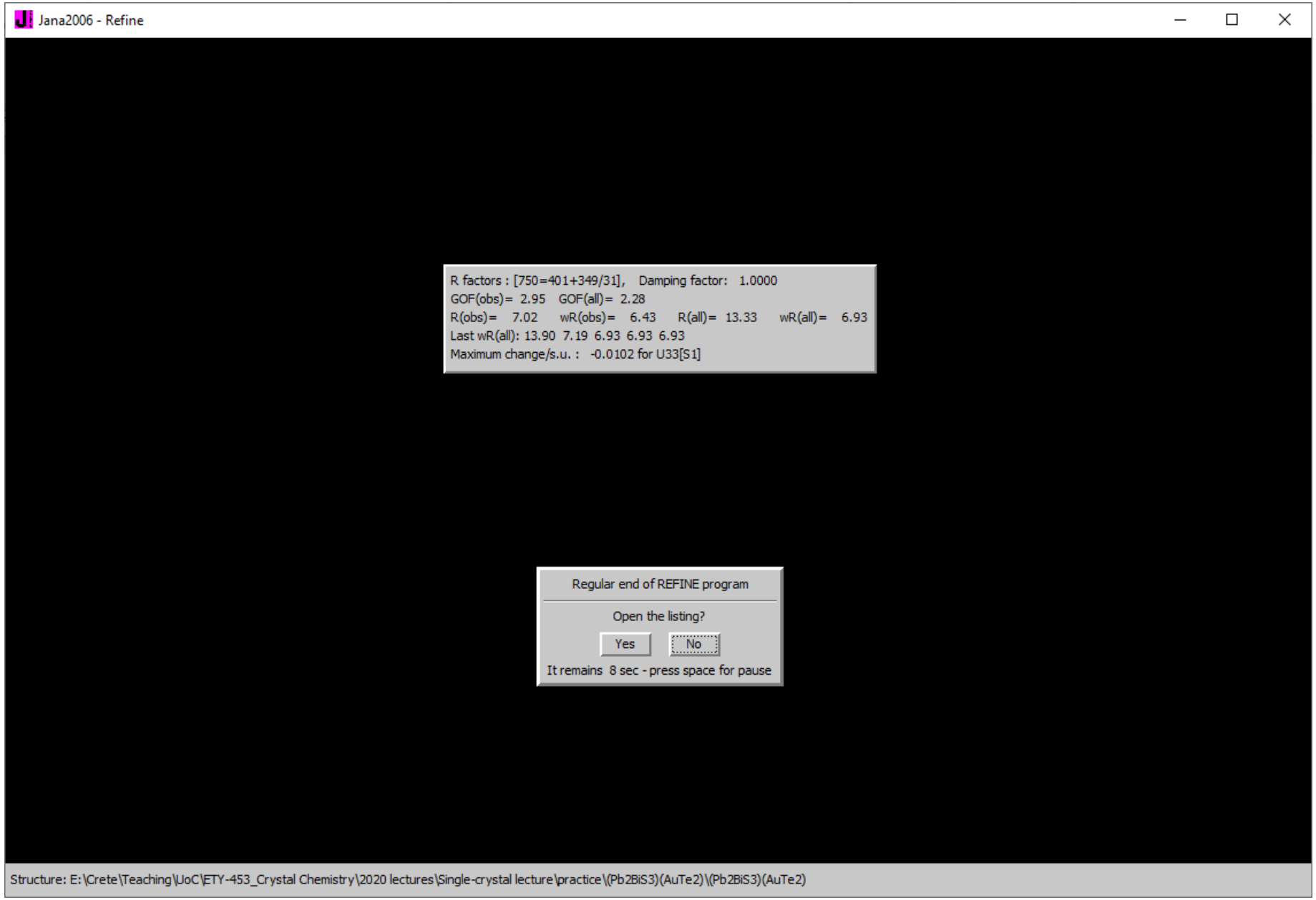


Once we have the structure and we are happy with the atoms, we start refining the thermal motions. This is very important when heavy atoms are present.

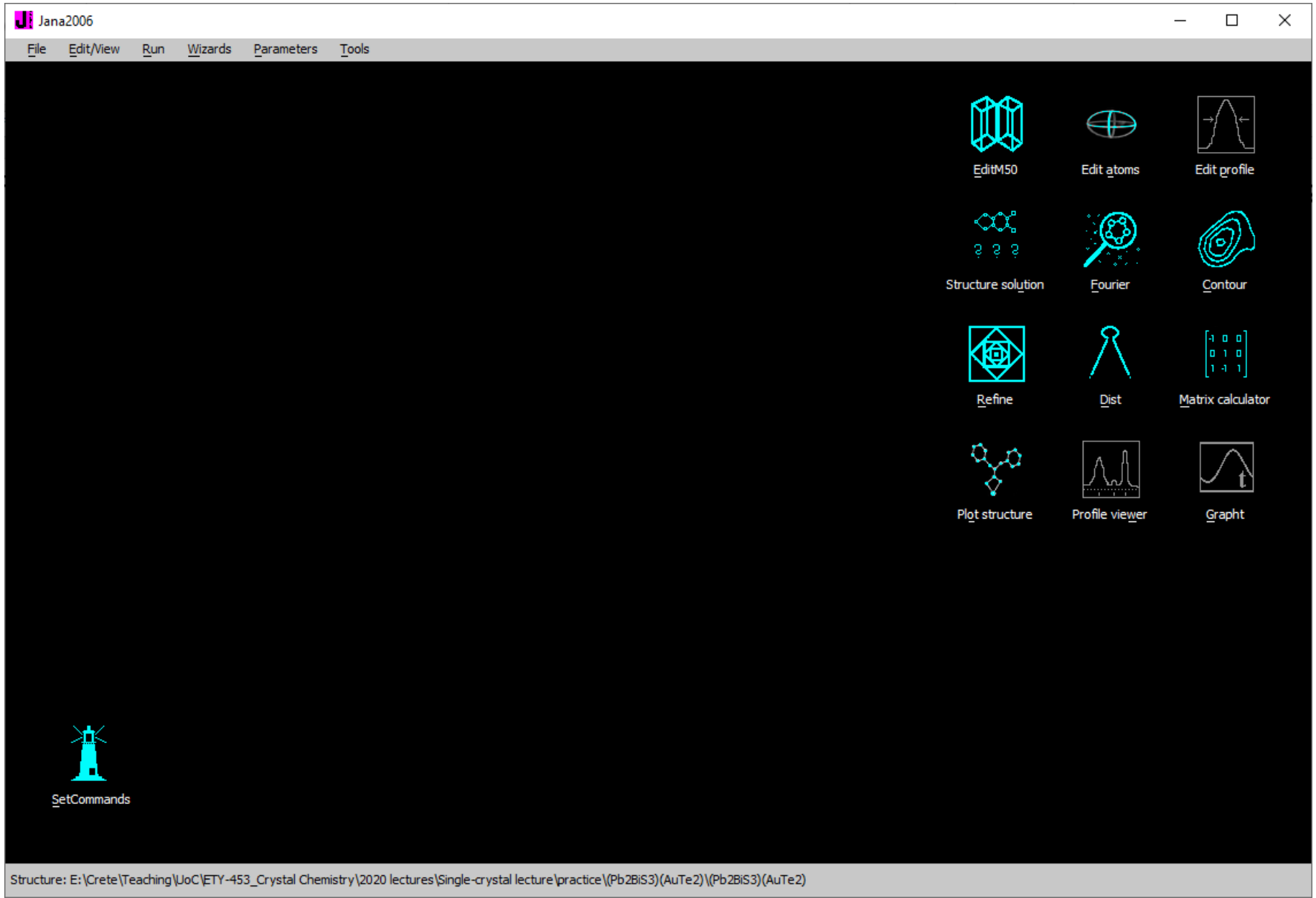




Refine again. Notice how the statistics improve drastically. With R<10% and wR<20%, you are about to complete the refinement. Hard part is done!

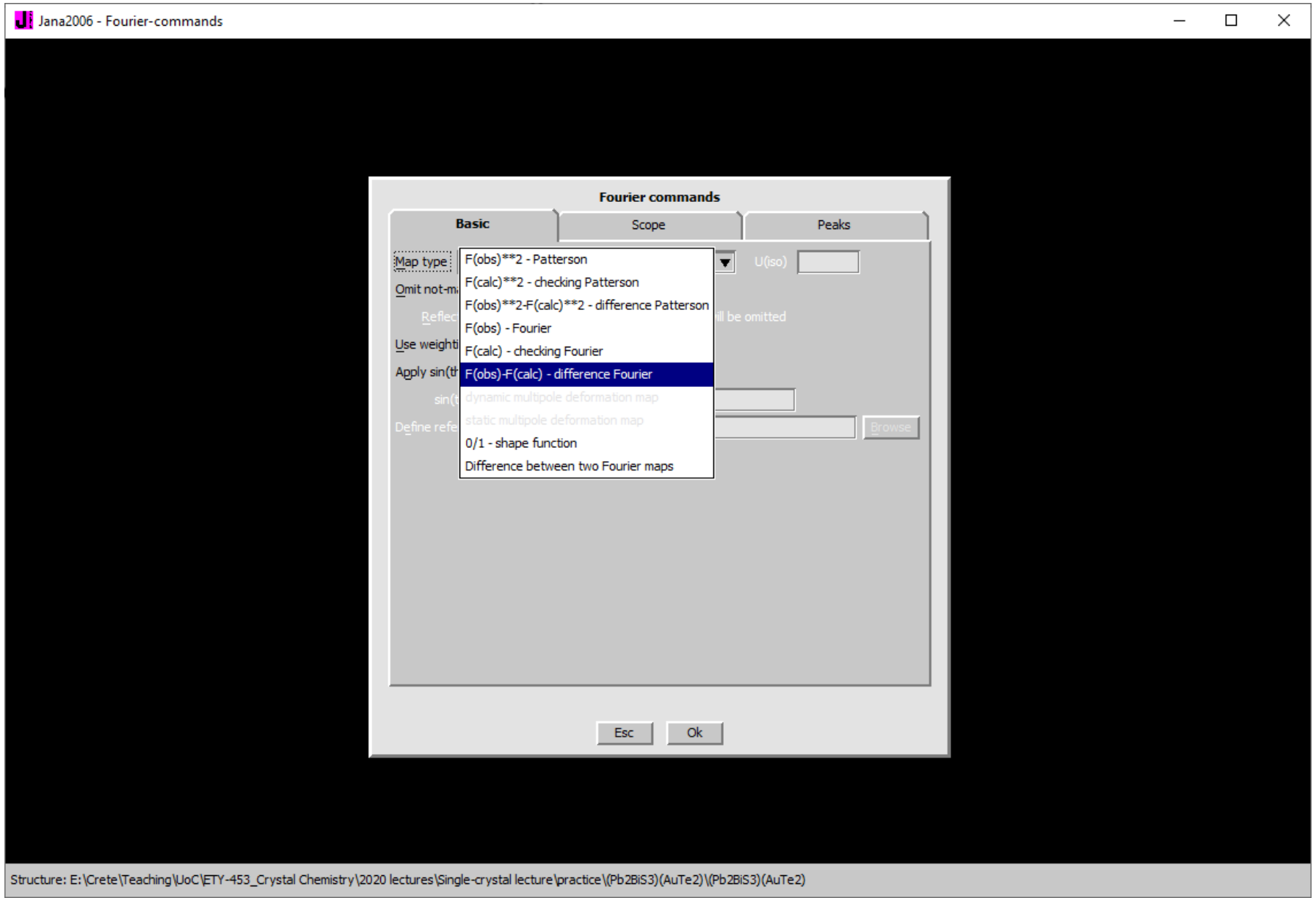


Before you finish. Make sure you check the details and right your files properly. First part is Fourier, followed by Dist

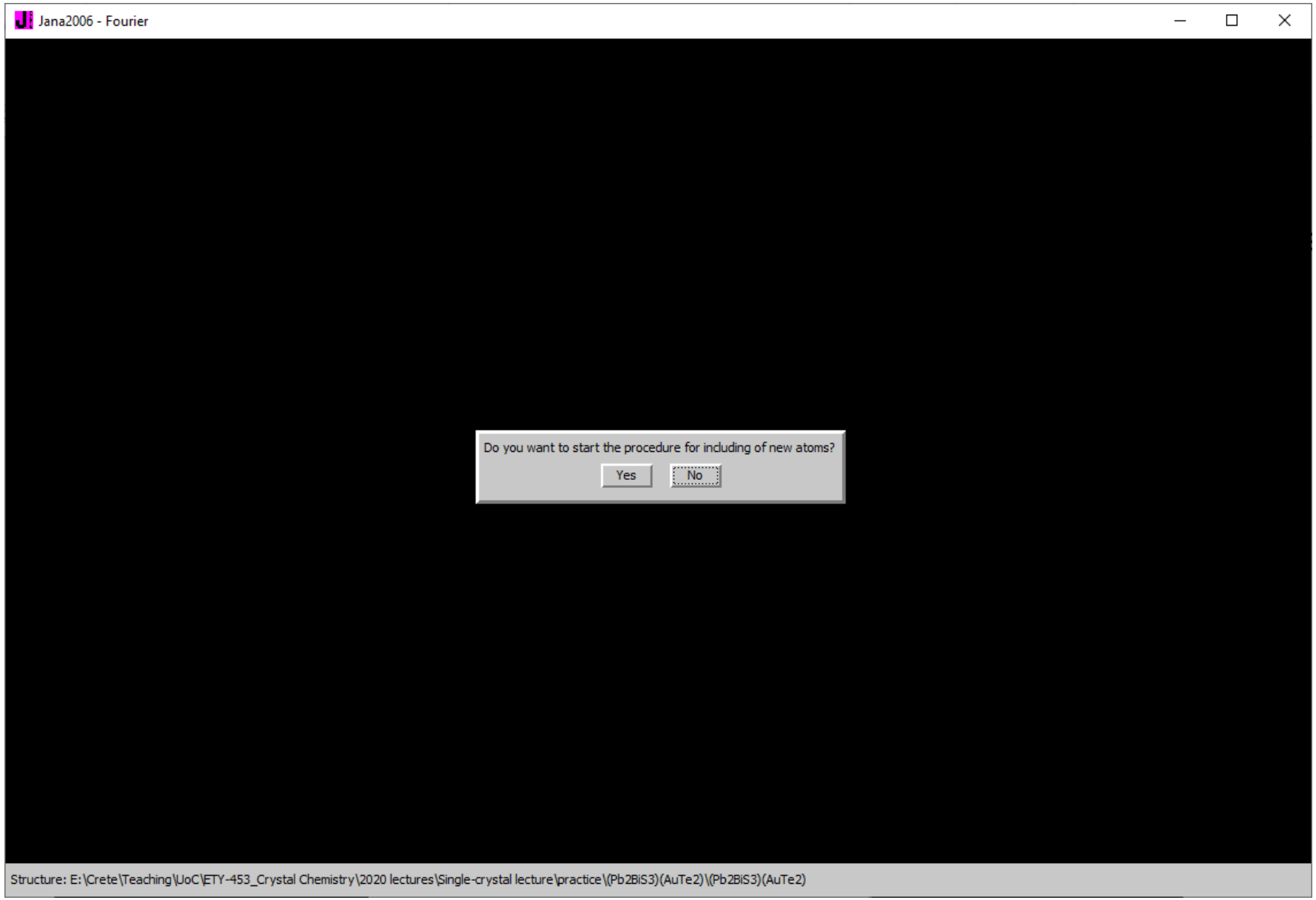


Run Fourier (right click)

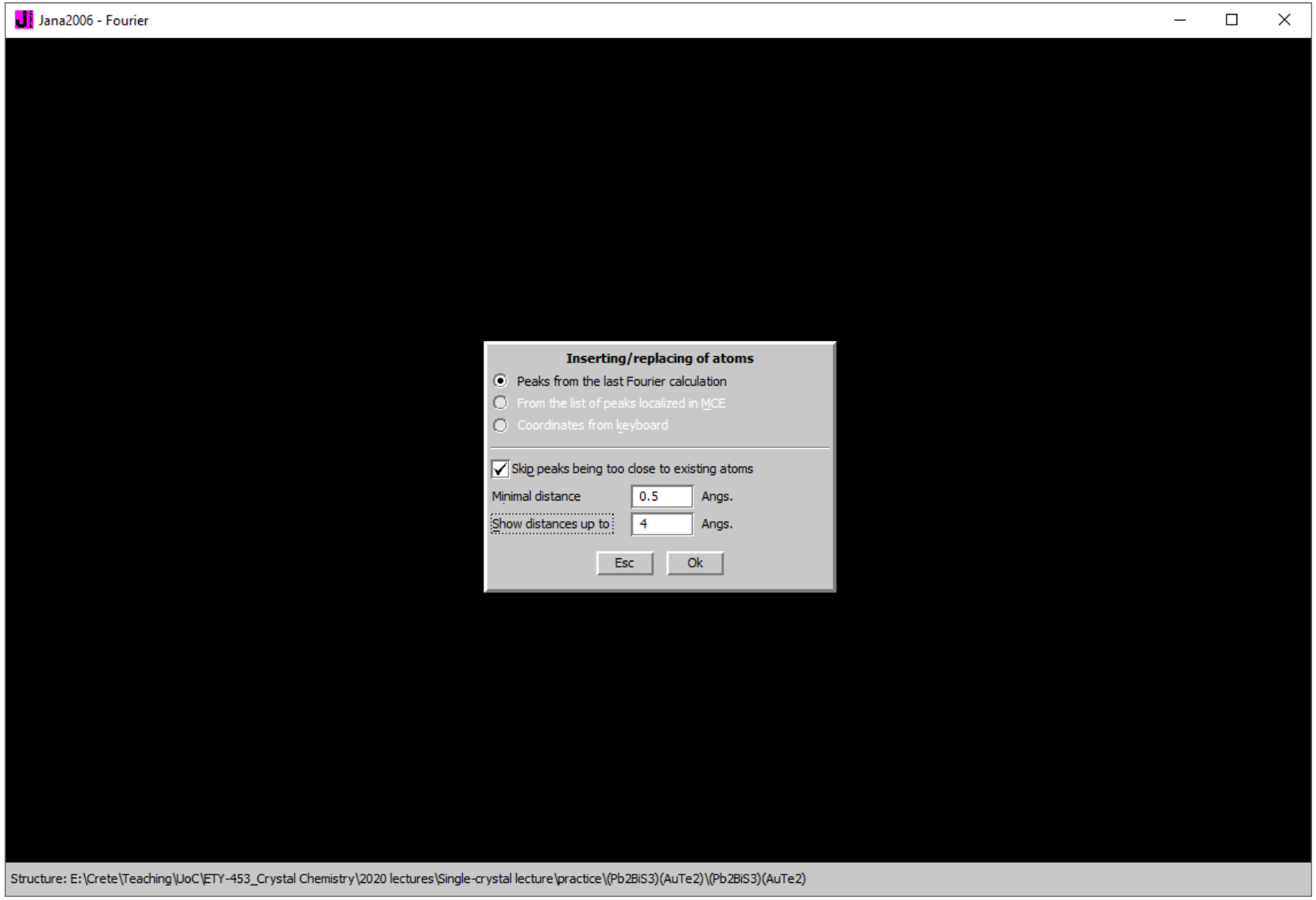
Select difference Fourier to assign unaccounted electron density to new atoms. Ok and start.



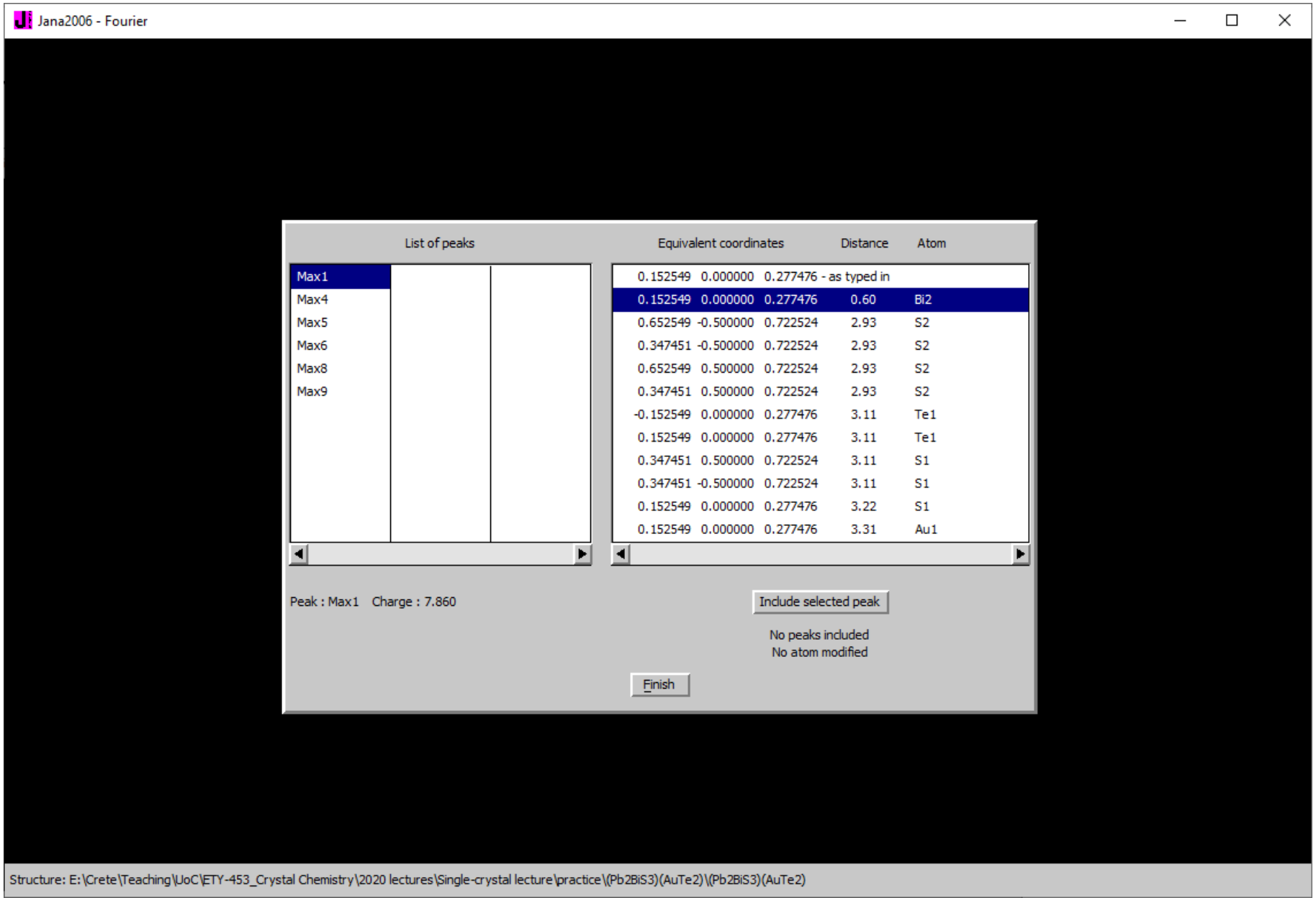
Select No. All the atoms are present.



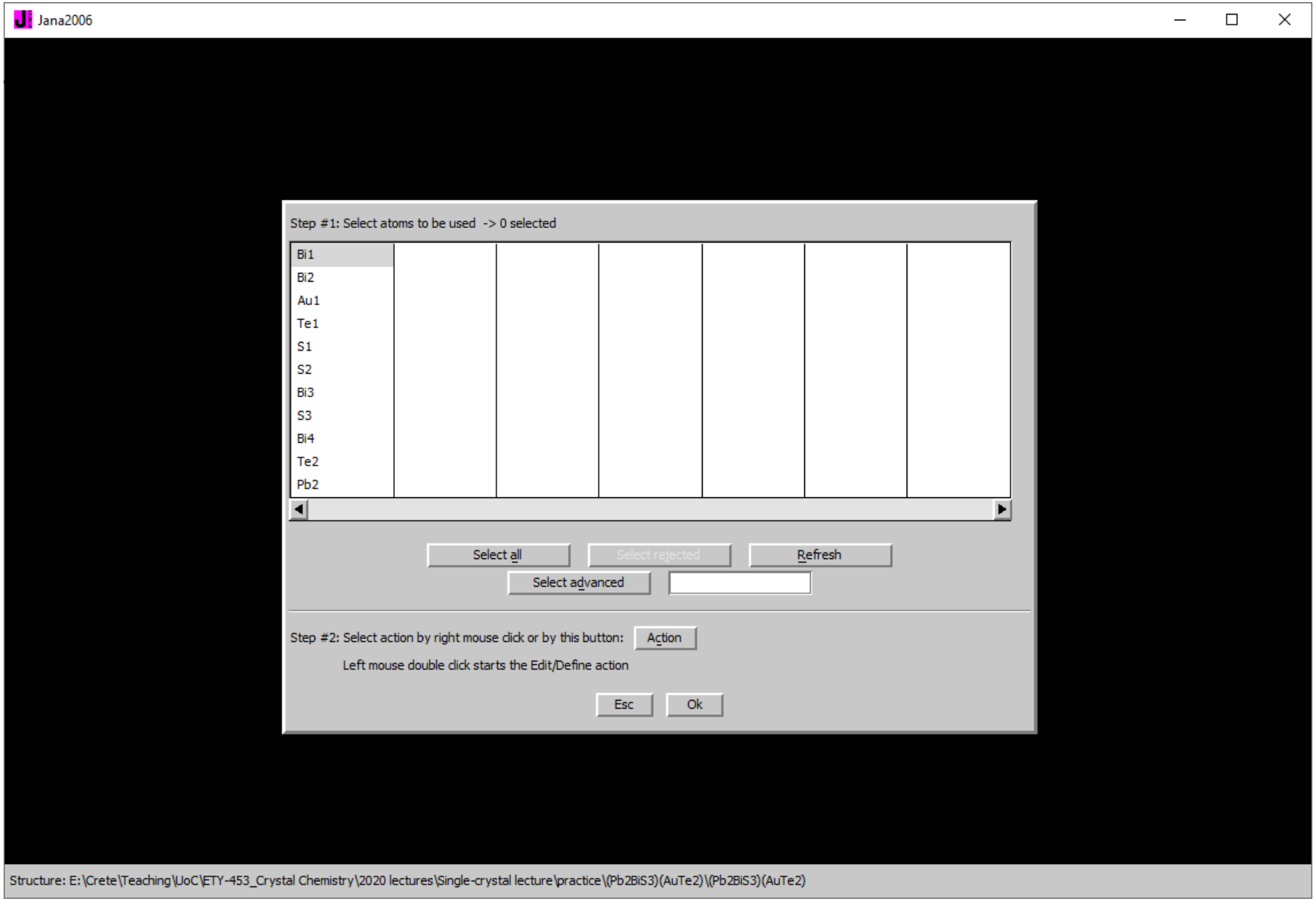
If there are atoms missing, you click yes on this menu. Choose to look for new atoms and select reasonable distances for new atoms. Not too close and slightly above what you expect for bonding distance



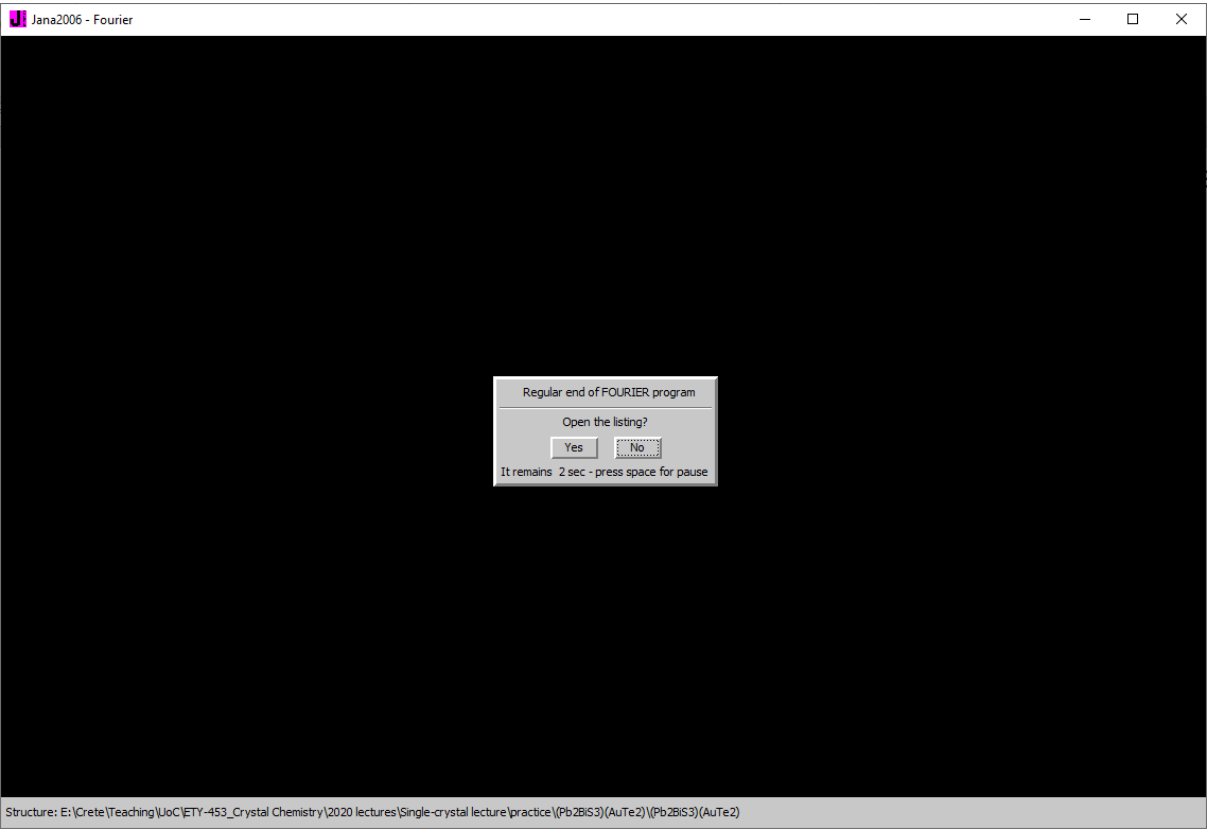
Include and name the new atoms. In this case, there is not appreciable density close to the atoms. Seems that all atoms have been found. No additions needed

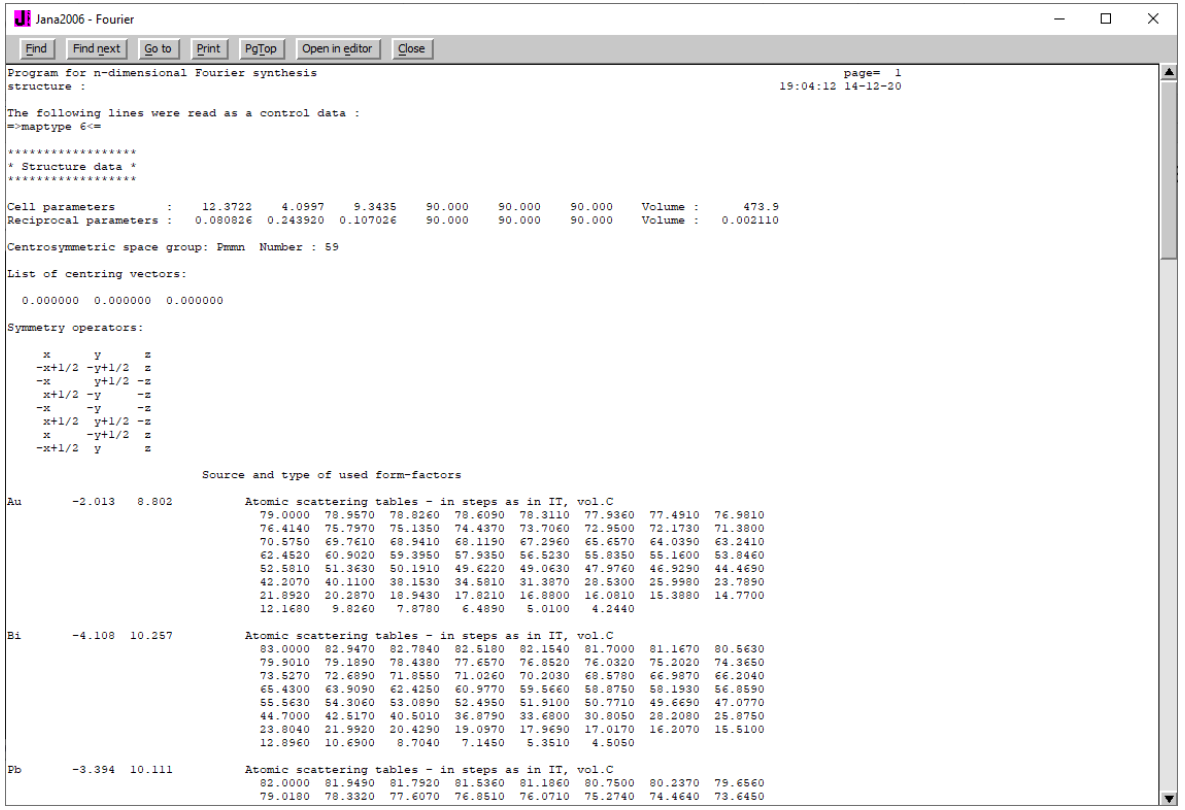


Now this is your new atom list. Modify, then, run refine again. And so on and so forth, until all atoms are present.



HOWEVER, in our case we have selected No. This is what comes out of Fourier.






```
Program for n-dimensional Fourier synthesis                                                    page=  1
structure :                                                                          19:04:12 14-12-20

The following lines were read as a control data :
=>maptype 6<=

******************
* Structure data *
******************

Cell parameters       :    12.3722    4.0997    9.3435    90.000    90.000    90.000    Volume :      473.9
Reciprocal parameters :   0.080826  0.243920  0.107026    90.000    90.000    90.000    Volume :   0.002110

Centrosymmetric space group: Pmmn  Number : 59

List of centring vectors:

  0.000000  0.000000  0.000000

Symmetry operators:

     x      y      z
    -x+1/2 -y+1/2  z
    -x      y+1/2 -z
     x+1/2 -y     -z
    -x     -y     -z
     x+1/2  y+1/2 -z
     x     -y+1/2  z
    -x+1/2  y      z

                          Source and type of used form-factors

Au       -2.013   8.802          Atomic scattering tables - in steps as in IT, vol.C
                                  79.0000  78.9570  78.8260  78.6090  78.3110  77.9360  77.4910  76.9810
                                  76.4140  75.7970  75.1350  74.4370  73.7060  72.9500  72.1730  71.3800
                                  70.5750  69.7610  68.9410  68.1190  67.2960  65.6570  64.0390  63.2410
                                  62.4520  60.9020  59.3950  57.9350  56.5230  55.8350  55.1600  53.8460
                                  52.5810  51.3630  50.1910  49.6220  49.0630  47.9760  46.9290  44.4690
                                  42.2070  40.1100  38.1530  34.5810  31.3870  28.5300  25.9980  23.7890
                                  21.8920  20.2870  18.9430  17.8210  16.8800  16.0810  15.3880  14.7700
                                  12.1680   9.8260   7.8780   6.4890   5.0100   4.2440

Bi       -4.108  10.257          Atomic scattering tables - in steps as in IT, vol.C
                                  83.0000  82.9470  82.7840  82.5180  82.1540  81.7000  81.1670  80.5630
                                  79.9010  79.1890  78.4380  77.6570  76.8520  76.0320  75.2020  74.3650
                                  73.5270  72.6890  71.8550  71.0260  70.2030  68.5780  66.9870  66.2040
                                  65.4300  63.9090  62.4250  60.9770  59.5660  58.8750  58.1930  56.8590
                                  55.5630  54.3060  53.0890  52.4950  51.9100  50.7710  49.6690  47.0770
                                  44.7000  42.5170  40.5010  36.8790  33.6800  30.8050  28.2080  25.8750
                                  23.8040  21.9520  20.4290  19.0970  17.9690  17.0170  16.2070  15.5100
                                  12.8960  10.6900   8.7040   7.1450   5.3510   4.5050

Pb       -3.394  10.111          Atomic scattering tables - in steps as in IT, vol.C
                                  82.0000  81.9490  81.7920  81.5360  81.1860  80.7500  80.2370  79.6560
                                  79.0180  78.3320  77.6070  76.8510  76.0710  75.2740  74.4640  73.6450
```

HOWEVER, in our case we have selected No. This is what comes out of Fourier.

Jana2006 - Fourier

Find | Find next | Go to | Print | PgTop | Open in editor | Close

	x	y	z	charge	rho	rel		x	y	z	charge	rho	rel
1.	0.2500	0.2500	0.0289	2.54	7.05	999	6.	0.5753	0.2500	0.7889	1.65	5.92	649
2.	0.5714	0.2500	0.5713	1.86	4.05	732	7.	0.4049	0.2500	0.0997	1.58	6.13	621
3.	0.5601	0.2500	0.9760	1.85	6.51	728	8.	0.7500	0.2500	0.8991	1.52	8.98	598
4.	0.5990	0.2500	0.0435	1.78	6.04	700	9.	0.2708	0.2500	0.7508	1.43	4.91	562
5.	0.2500	0.2500	0.5124	1.73	3.98	680	10.	0.5923	0.2500	0.9138	1.42	3.98	559

This is what you are looking for. Unaccounted electron density (in e/Å^3 units).
It is positive for electron deficit

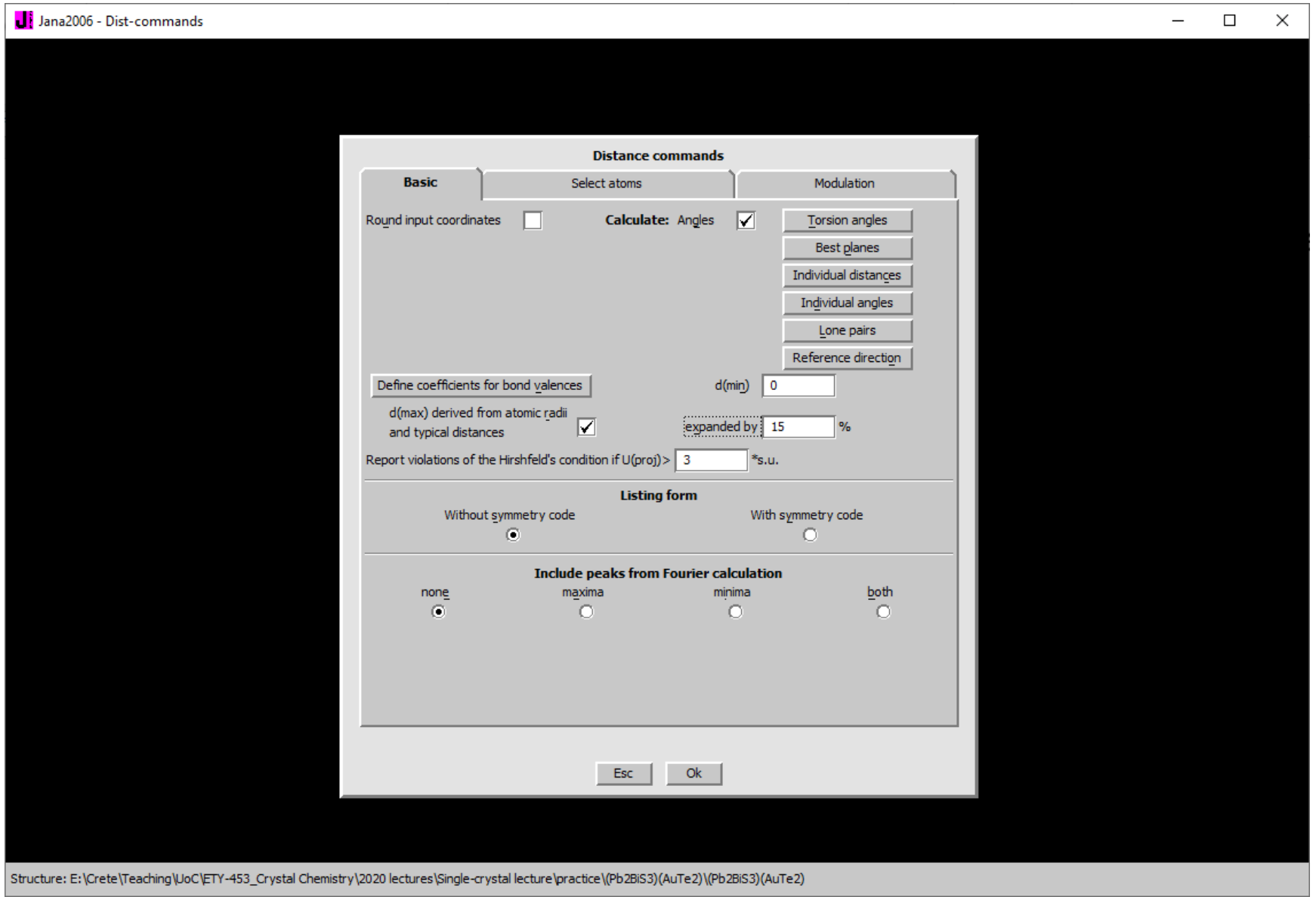
…and negative for electron excess (list below)

```
Program for n-dimensional Fourier synthesis                                    page=  4
structure :                                                          19:04:12 14-12-20


Searching for negative peaks - maximum number of peaks to be found :  10

The list of negative peaks written to the m40  file
```

Run Dist (right click)

Select all the parameters that you want to be written in your final .cif file.

Click ok and start the program.



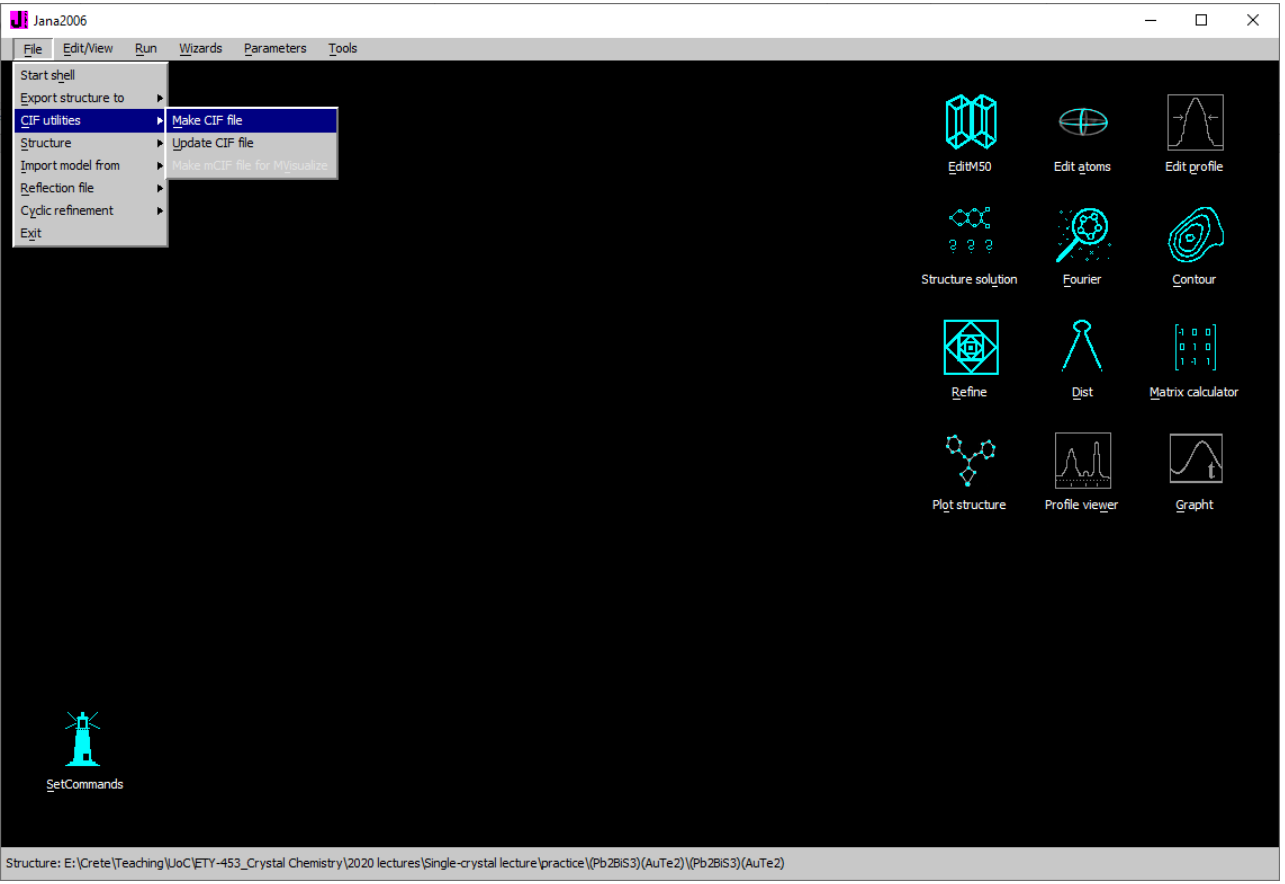
This is the Dist output file. Bond angles and bond distances are included.

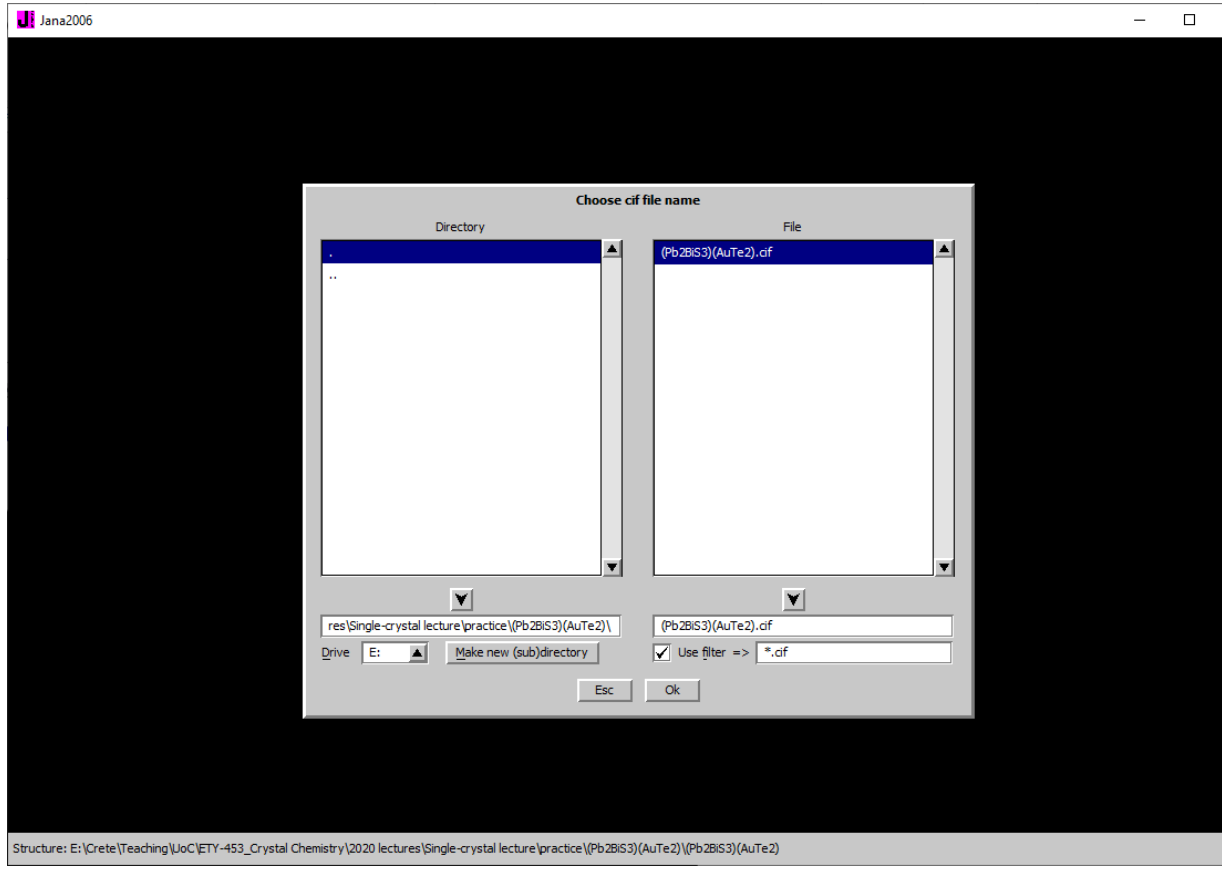
Jana2006 - Dist

Find | Find next | Go to | Print | PgTop | Open in editor | Close

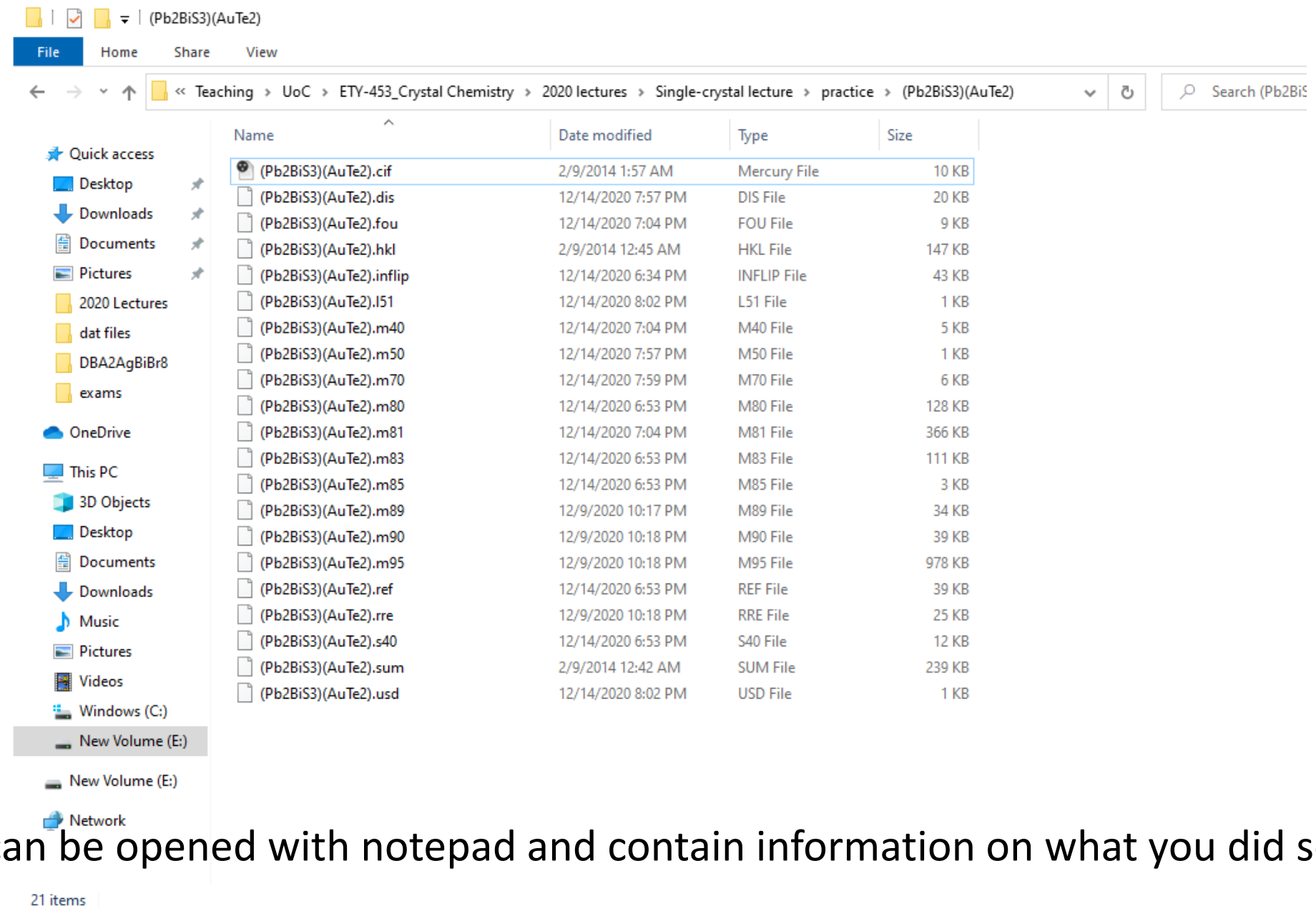
```
Distances and angles will be calculated from d(min)=   0.000 to specific maximal distances as listed below expanded by 15%:

Au-Au 2.880 R     Au-Bi 3.260 R     Au-Pb 3.190 R     Au-S  2.341 T     Au-Te 2.810 R
Bi-Bi 3.640 R     Bi-Pb 3.570 R     Bi-S  2.631 T     Bi-Te 3.190 R
Pb-Pb 3.500 R     Pb-S  2.744 T     Pb-Te 3.120 R
S-S   2.080 R     S-Te  2.410 R
Te-Te 2.740 R

T ... typical distances taken either from the file distributed with Jana program or defined by user
R ... distance as derived from atomic radii:

                                        Atom type    Atom radius
                                          Au            1.440
                                          Bi            1.820
                                          Pb            1.750
                                          S             1.040
                                          Te            1.370

*************************       S2.........80.9(4)            S2.........134.9(2)           S2.........84.0(2)
* atom Au               *       S2.........89.1(2)          Pb...........4.081(3)           S2.........84.0(2)
*************************       S2.........160.5(5)           Bi.........90.000(5)        S2...........2.906(10)
Te1.........2.7150(19)        S1...........2.974(4)           Bi.........90.000(5)          S2.........89.7(3)
  Te1.......98.05(6)            S2.........80.9(4)            S1.........93.99(6)           S2.........89.0(3)
  Te1.......81.94(6)            S2.........160.5(5)           S2.........134.9(2)           S2.........167.9(4)
  Te1.......179.17(18)          S2.........89.1(2)            S2.........134.9(2)         S2...........2.906(10)
Te1.........2.7150(19)        S2...........2.794(12)          S2.........46.2(2)            S2.........167.9(4)
  Te1.......179.17(18)          S2.........79.6(3)            S2.........46.2(2)            S2.........89.0(3)
  Te1.......81.94(6)            S2.........79.6(3)          Bi...........4.0997(14)       S2...........2.906(10)
Te1.........2.7150(19)        S2...........2.947(11)          Bi.........**                 S2.........89.7(3)
  Te1.......98.05(6)            S2.........88.1(3)            S1.........90.00(7)         S2...........2.906(10)
Te1.........2.7150(19)        S2...........2.947(11)          S2.........45.1(2)          *
*                             *                               S2.........134.9(2)         *************************
*************************     *************************       S2.........45.1(2)          * atom Te1              *
* atom Pb               *     * atom Bi             *         S2.........134.9(2)         *************************
*************************     *************************     Bi...........4.0997(14)       Au...........2.7150(19)
Bi...........4.081(3)         Pb...........4.081(3)           S1.........90.00(7)           Au.........98.05(9)
  S1.........134.42(10)         Pb.........172.02(10)         S2.........134.9(2)         Au...........2.7150(19)
  S1.........134.42(10)         Bi.........90.000(5)          S2.........45.1(2)          *
  S2.........87.6(3)            Bi.........90.000(5)          S2.........134.9(2)         *************************
  S2.........45.4(2)            S1.........93.99(6)           S2.........45.1(2)          * atom S1               *
  S2.........45.4(2)            S2.........46.2(2)          S1...........2.69(2)          *************************
S1...........2.974(4)           S2.........46.2(2)            S2.........84.0(2)          Pb...........2.974(4)
  S1.........87.13(11)          S2.........134.9(2)           S2.........84.0(2)            Pb.........87.13(12)
Calculating of distances, angles, torsion angles and best planes                                          page=  4
structure :                                                                                    19:57:01 14-12-20

  Pb.........90.68(12)
  Pb.........164.1(8)
  Bi.........97.9(4)
Pb...........2.974(4)
  Pb.........164.1(8)
  Pb.........90.68(12)
  Bi.........97.9(4)
Pb...........2.974(4)
  Pb.........87.13(12)
```

Finalize the structure by making a .cif file. All your work is written in this single file.



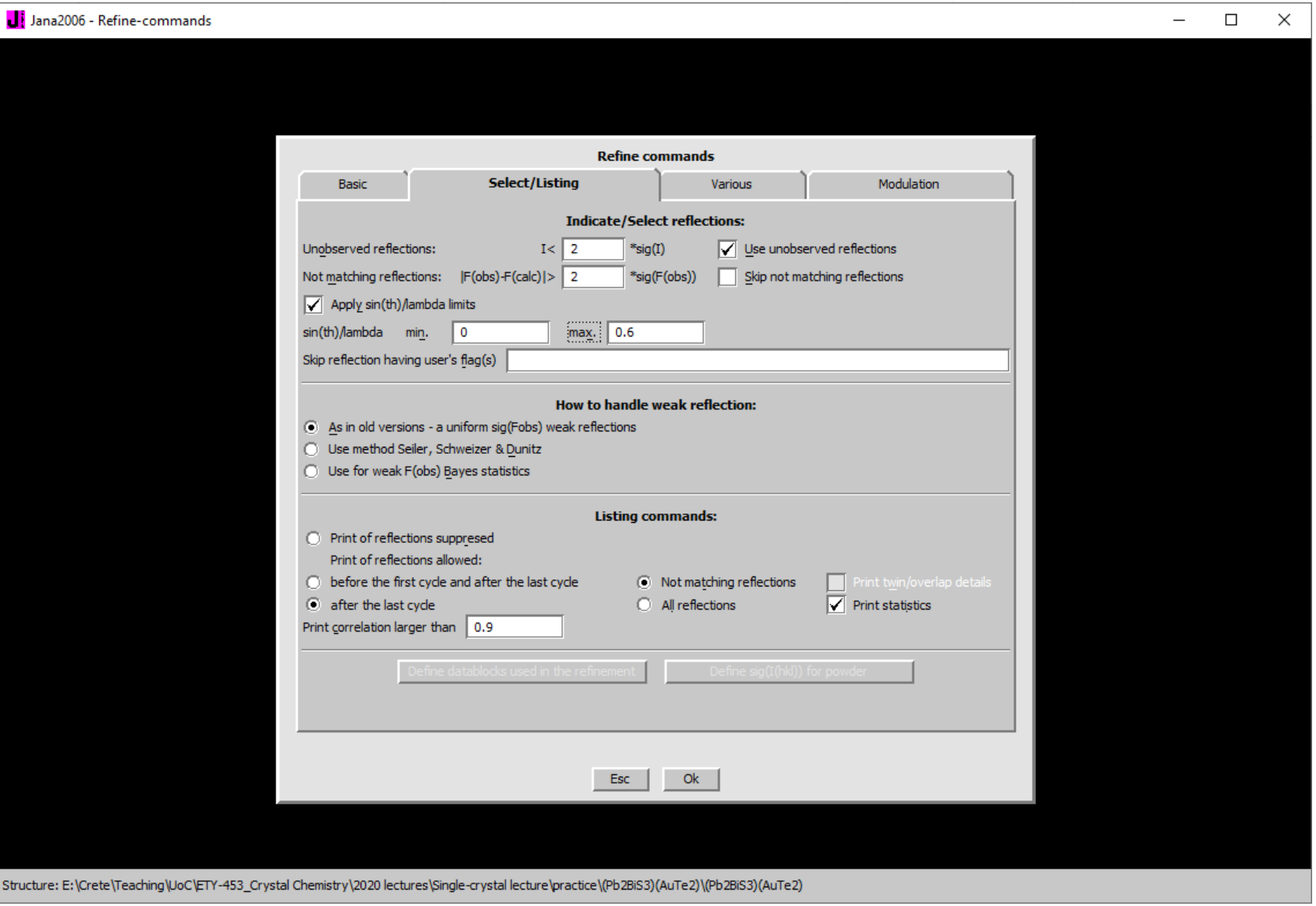


This is how your folder should look like once you are done.



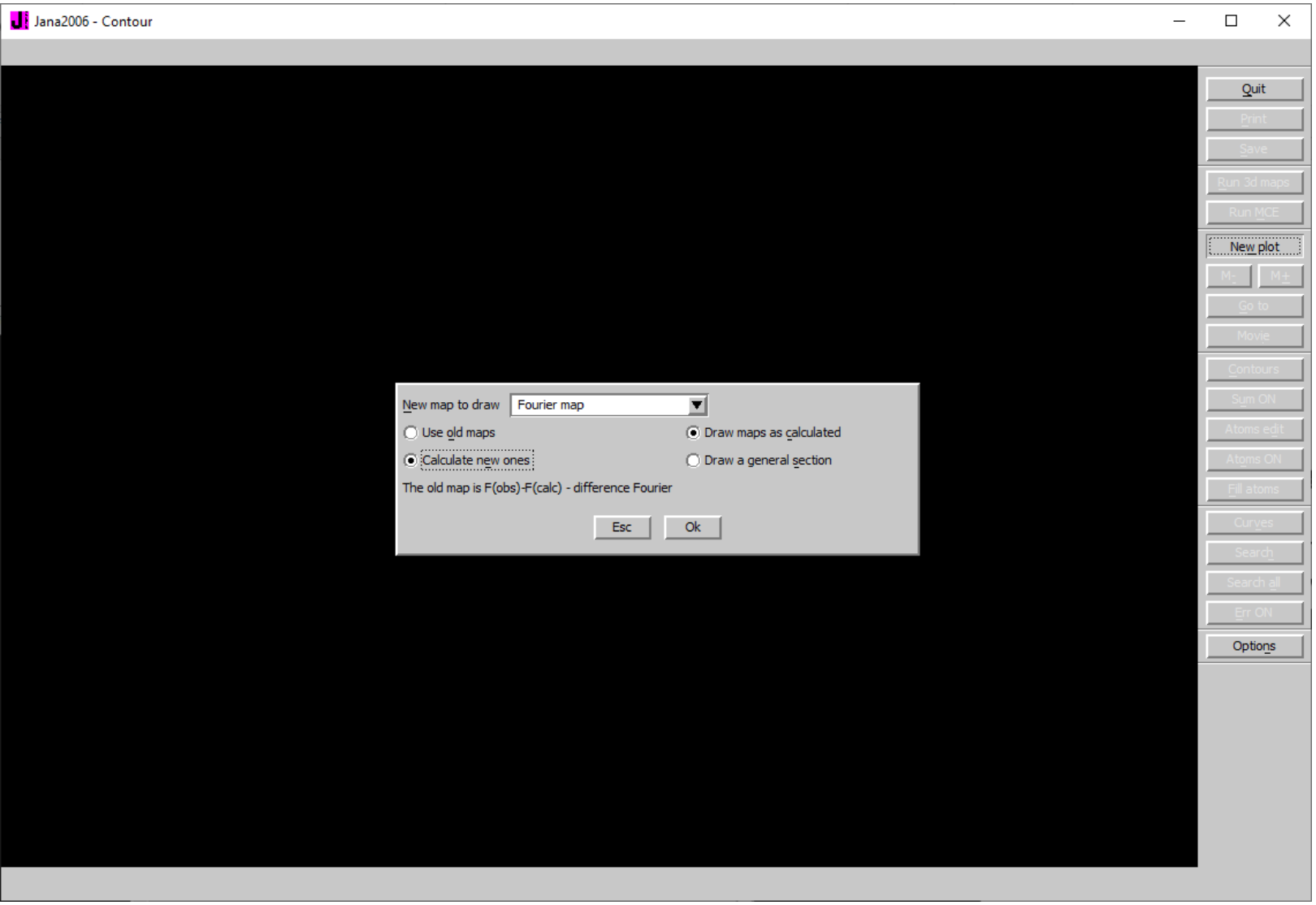
All files can be opened with notepad and contain information on what you did so far.

Tweaks and Tricks



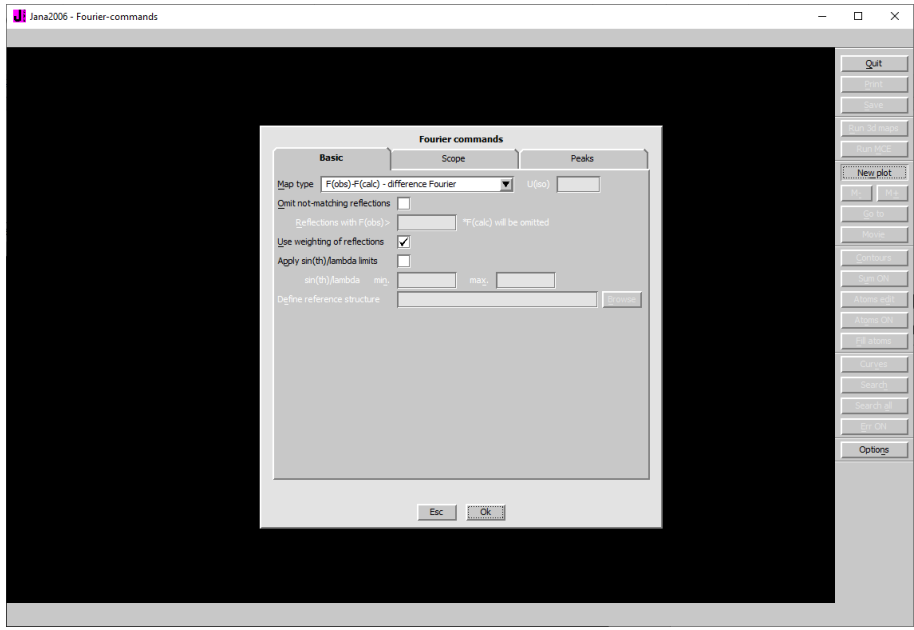
If your data are bad, or there is no intensity at high 2θ angles, then you can eliminate these data. You do this by making the sin(θ)/λ term to correspond to 2θ ~50° (θ = 25°) for the wavelength you are using. This will immediately omit all data above this angle.

The Fourier map. Contour plot command

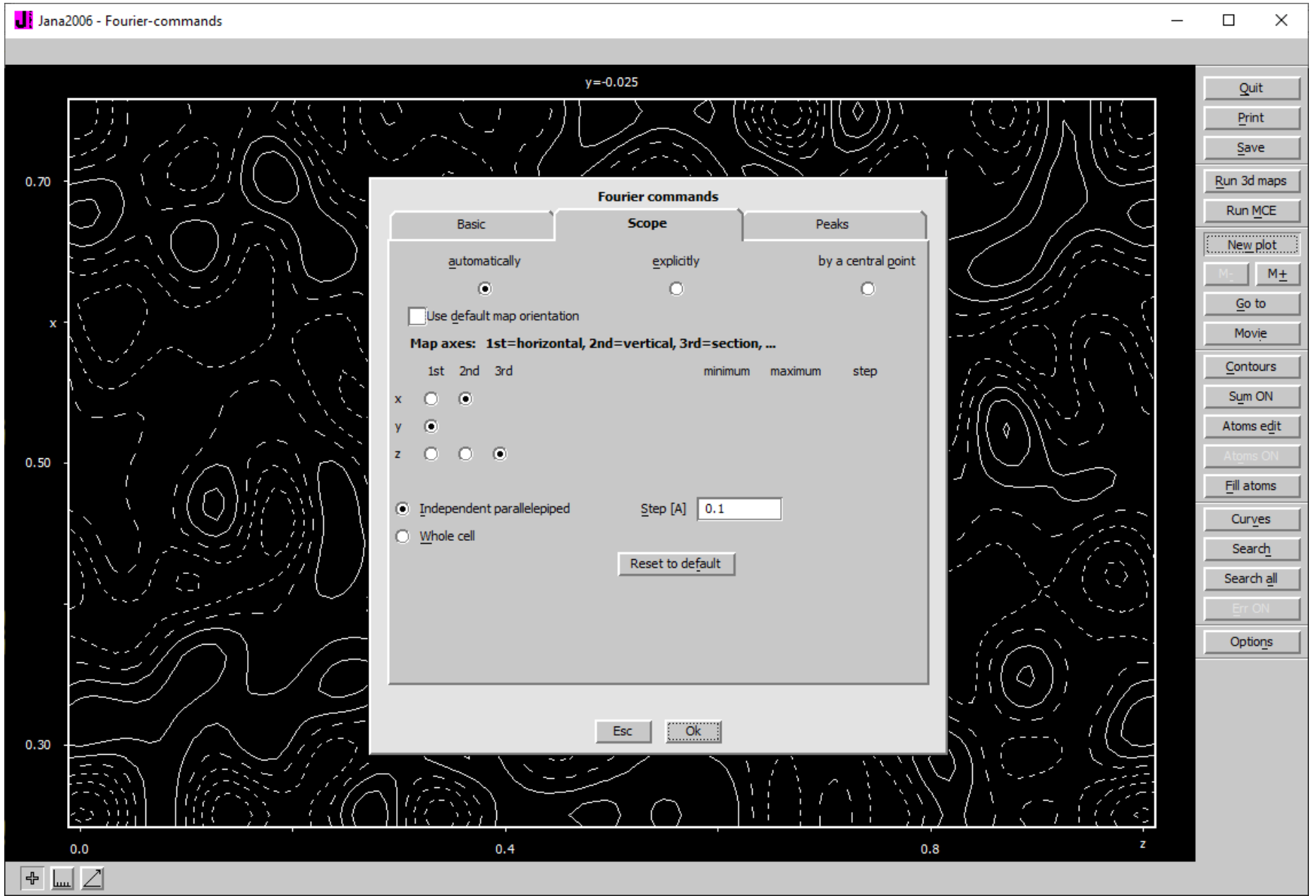


Click the contour icon and select calculate new ones in the next menu.

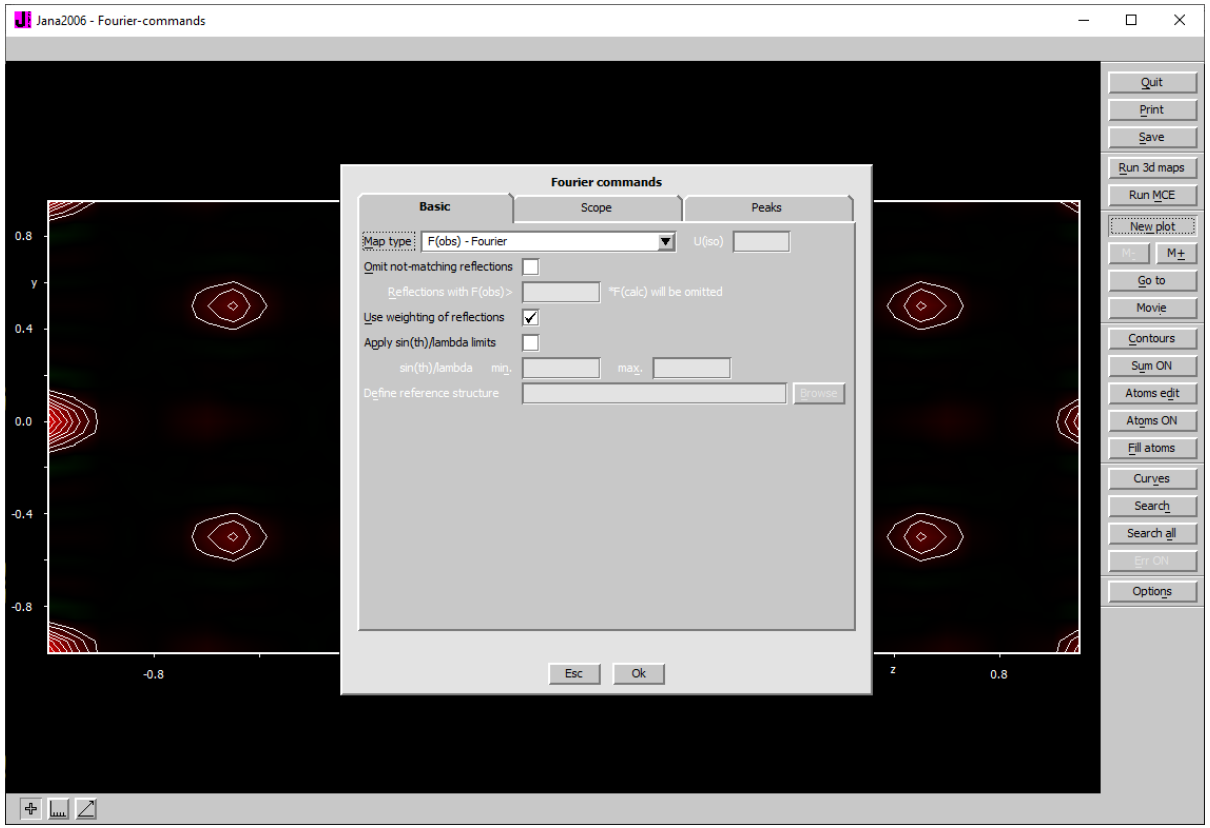
Accept the changes in the menu after that.

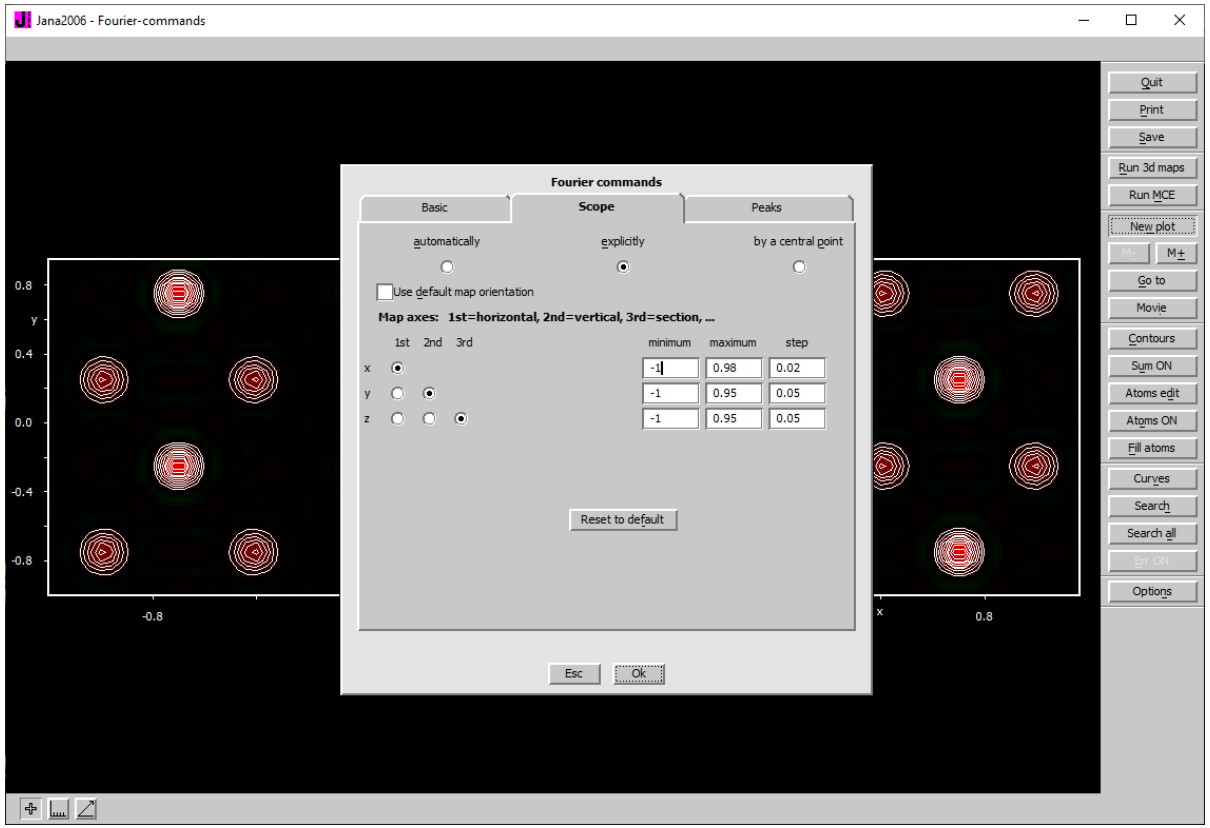


You can open the menu again using the new plot command. Choose the scope to orient the unit cell in the direction of your choice. You want to see the unit cell along the a-axis in this example



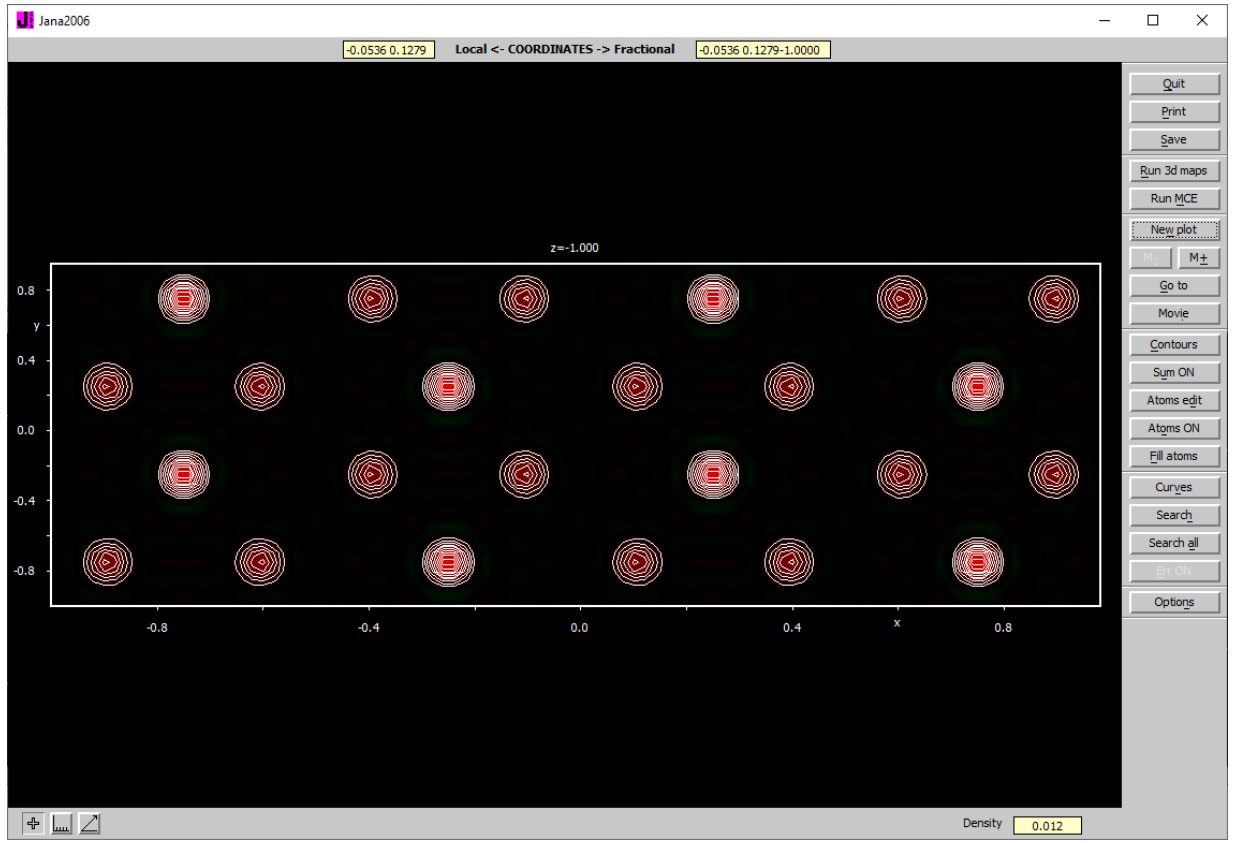
Run a difference Fourier map and select a 2x2x2 supercell viewed along the a-axis





This is the electron density map of the $[AuTe_2]^-$ layer

Fourier map (electron density on the atoms)



Difference Fourier map (electron density on not on the atoms)