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Sequential SHELXL refinement of consecutively collected datasets: A tool to probe the dynamic evolution of single crystal structures

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Modern area detectors combined with bright synchrotron radiation allow for high speed collection of both powder and single crystal data with high time resolution studying changing external conditions e.g. P or T. Such experiments are hitherto more common for powder diffraction where crystal properties analyses for a large number of datasets are easily done using sequential or parametric refinement with e.g. FullProf or TOPAS. Here we present a similar procedure for single crystals experiments based on continuous data collection and sequential use of SHELXL and the subsequent extraction of data items.

Basic assumption: the temperature of any external stimuli step is small, and there is no phase transition.
Expectations: inherited parameters, e.g. atomic positions and ADPs, serve as good starting model for the succeeding data point

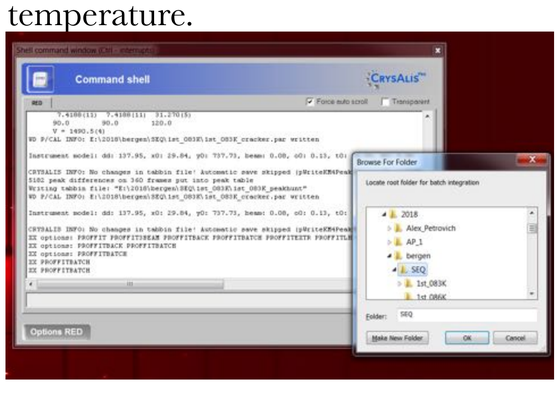
Experimental example: from BM01 SNBL at the ESRF Pilatus@SNBL diffractometer[2], Spin crossover in $[Fe(tame)_2]Br_2 \cdot MeOH$.[6] 60 full sphere single crystal 360 sec. data sets collected with a 3K temperature interval on cooling from 260 to 83K. Every dataset is a collection of raw frames stored in separate folders. Space group R-3m.

1. Data pre-processing: SNBL ToolBox [2]

At this step we prepare files for data processing keeping the same experimental parameters for all data sets.

2.Data processing: Crysalis [3]

First, process 1st dataset separately under human control, and then use macros for sequential processing. Crysalis makes sequential data processing using predefined UB matrix and parameters of the experiment. UB is refined at every point and transferred to the next temperature.



3. Structure solution. SHELXT[1]

Solve and refine the structure from 1st dataset

4. Sequential SHELXL [4]

```
E:\2018\bergen\SEQ>seq_shel.exe shelx /r E:\2018\bergen\SEQ\1st_083K\struct\tmp\
1st_083K.res
```

run seq_shel.exe in the parent folder with /r [where the first *.res file is stored]
The software does the following:

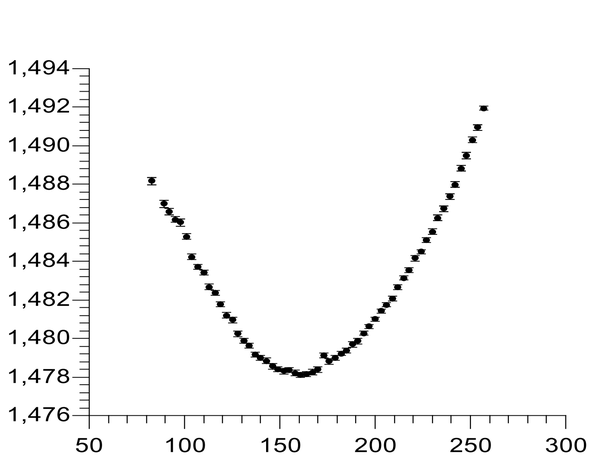
1. Copies *.res to *.ins for the next temperature.
2. Updates the unit cell dimensions from CrysAlis par file
3. Runs SHELXL
4. Repeats steps 1-4 till the end

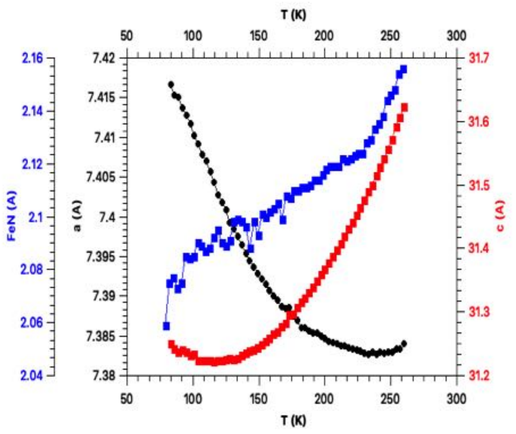
5. Extracting the data [5]

```
E:\2018\bergen\SEQ>seq_shel.exe cell
```

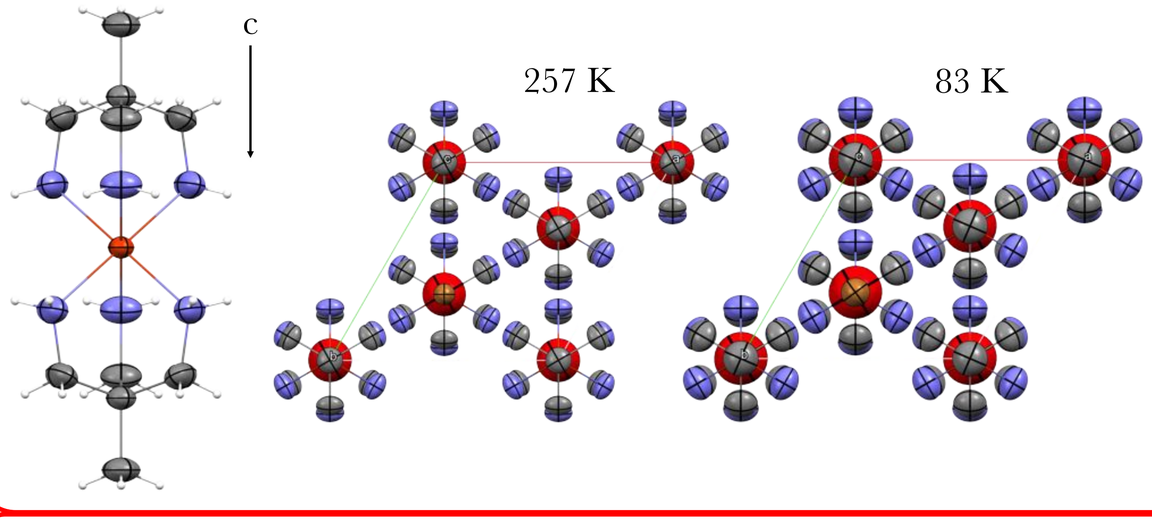
This command creates cell.dat: unit cell dimensions vs. temperature.
The software also can extract numerical information from any specific line of the CIFs for tables or plots.

A gradual Spin Crossover with negative thermal expansion below 150K.





We detect an anisotropic negative thermal expansion. On cooling, there is a decrease of Fe-N bond length indicative of the High Spin→Low Spin conversion, but accompanied by an increase of ADPs manifesting a growing disorder and an associated volume increase. The reciprocal space shows no obvious trace of diffuse scattering indicating that the HS and LS spin state distribution of complexes is essentially uncorrelated. The origin of the lattice anomalies may therefore be linked to a spin state disorder of $[Fe(tame)_2]^{2+}$.



1. G. M. Sheldrick (**2015**). Acta Cryst. C71, 3-8
2. Dyadkin, V., Pattison, P., Dmitriev, V. & Chernyshov, D. (**2016**). J. Synch. Rad. 23, 825–829
3. https://www.rigaku.com/en/products/smc/crysalis
4. G. M. Sheldrick (**2015**). Acta Cryst. A71, 3-8
5. www.soft.snbl.eu [seq_shel]
6. Bernhardt et al. Chem Eur. J. (**2018**), 24, 5082-5085

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