Symmetry mode based parametric Rietveld refinement of the structural phase transition of $CuInSe_2$

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Symmetry modes provide an alternative method to describe crystal structures. Using the fact that many crystal structures can be described as a distorted version of a higher symmetric parent structure, the traditional atomic positions, occupancies or lattice parameters are no longer used. Instead, all structural features are described applying symmetry modes. This can be of particular interest if structural changes during a real phase transition are studied. The symmetry modes of one given type belonging to the same irreducible representation (irrep) comprise an order parameter. The decomposition of a crystal structure in terms of symmetry modes can nowadays be done using web-based software programs like ISODISTORT (http://stokes.byu.edu/isodistort.html) or AMPLIMODES (http://www.cryst.ehu.es/cryst/amplimodes.html)

The behaviour of an order parameter over a phase transition can be conveniently described using Landau theory. Within Landau theory the thermodynamic state of the system and the free-energy difference that stabilizes the low-symmetry phase (the excess Gibbs free energy) are described in terms of thermodynamic order parameters. In case of a second-order (a.k.a. continuous) phase transition, the order parameters have a value of zero in the high symmetry phase and increase continuously after the temperature T falls below the transition temperature T_{crit}, whereas for first-order (a.k.a. hysteretic) phase transitions an order parameter can abruptly "jump" to a non-zero value. The order parameter's dependence on temperature T can be modelled satisfactorily by an empirical power law of the form:

$$Q = f\left|T - T_{crit}\right|^{\beta}, \qquad (1)$$

where β is the critical exponent, and f is a power law coefficient. Typical values of β are ½ for ordinary scalar second-order transitions, or ¼ for a transition at the tricritical point that marks the boundary between first and second-order transitions.

Parametric Rietveld refinement offers great possibilities in the study of symmetry modes and order parameters from *in-situ* powder diffraction data. Instead of refining a series of powder patterns independently and fitting an empirical or physical model to refined values, the functional dependency is introduced in the refinement and the parameters of the function are refined directly. The benefit of parametric Rietveld refinement in comparison to traditional sequential Rietveld refinement is that the correlation between parameters and the final standard uncertainty can be reduced and simple physically meaningful constraints and restraints can be introduced.

$CuInSe_2$ shows a ferroelastic phase transition from a tetragonal (space group $I\bar{4}2d$) low-symmetry structure to a cubic (space group $F\bar{4}3m$) parent structure at a temperature of 808 °C. The low symmetry structure is formed by a doubling of the cubic parent structure in one direction (denoted as c-axis) and a slight tetragonal distortion causing an elongation of the c-axis and consequently a compression of the a-axis (Fig. 1). Additionally, the position of the selenium atom changes from a special (4c, $F\bar{4}3m$) to a more general Wyckoff position (24g, $I\bar{4}2d$, which is equal to the Wyckoff position 8d in space group $F\bar{4}3m$). In the low symmetry phase copper and indium occupy distinct positions (Wyckoff position 4a and 4c respectively), while in the high symmetry phase they are occupationally disordered at those positions.

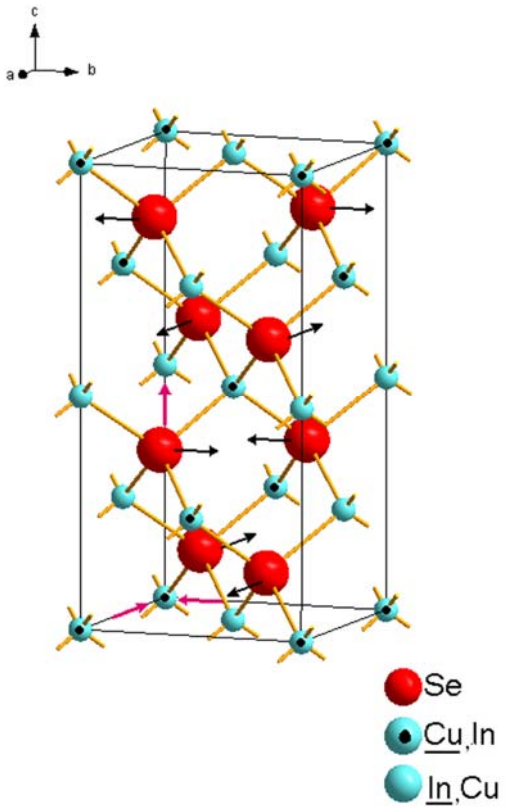

Figure 1: Crystal structure of tetragonal $CuInSe_2$. The pink arrows indicate the directions of the tetragonal distortion; the black arrows indicate the movement of the selenium atoms (red). The two different cation positions are given by blue atoms. Cation position 1 (Wyckoff position 4a; $I\bar{4}2d$) ((blue atom with black dot) is preferred by copper, while cation position 2 (Wyckoff position 4b; $I\bar{4}2d$) (blue atoms) is preferred by indium in the low symmetry phase).

In order to describe these changes within the crystal structure three different types of symmetry modes are necessary. Two strain modes *s1* and *s2* are able to model the changes of the lattice parameters; one displacive mode *a1* is responsible for the position of the selenium atom and an occupancy mode causes the ordering of copper and indium atoms to distinct crystallographic positions within the low symmetry structure. The ISODISTORT software was used to obtain a set of equations which connect the symmetry mode amplitudes and the individual structural parameters.

For Rietveld refinement, temperature dependent powder diffraction data of $CuInSe_2$ were recorded at the ID15B high energy beamline at the ESRF synchrotron radiation facility in Grenoble, France. The sample was prepared by solid state reaction and sealed in a silica tube to prevent evaporation. During the measurement the sample was heated from 300 °C to 875 °C, and one measurement was performed every degree. Further experimental details can be found in Schorr & Geandier [1].

For parameterisation of the symmetry modes, the measured temperature range was divided into three sections: a low temperature range (tetragonal space group), the transition region, and a high-temperature range (cubic space group). Linear functions, power law behaviour (1) and refineable or fixed values were used in order to model the behaviour of the symmetry modes.

Symmetry mode based Rietveld refinements were performed in sequential and parametric manner. A plot of the parametric refinement is shown in Fig. 2. Almost flat difference plots indicate that the fits are satisfactory both in the sequential as well as in the parametric Rietveld refinement. A comparison of the R_{wp} values for both types of refinement shows that the same quality of fits is obtained.

All four parameters *a1*, *s1*, *s2* and *occ* could be modelled in good agreement with the values obtained for sequential Rietveld refinement (Fig. 3). In case of sequential refinement the *a1* parameter shows a slight deviation form the ideal value of zero in the cubic phase, though this only causes a deviation in the *x*-position of the Se atom of 0.004. The *s2* parameter shows large values for the estimated standard deviations (esd's) in the cubic phase.

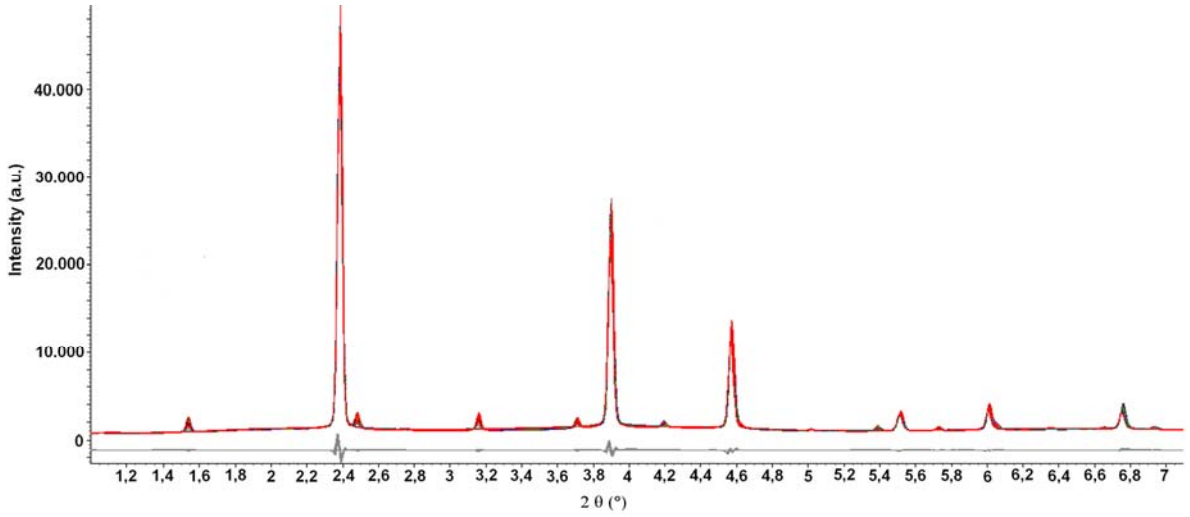

Figure 2: Plot of the parametric Rietveld refinement of the phase transition of CuInSe2 in the temperature range from 786 °C to 828 °C. Observed and calculated intensities and their differences are plotted for all temperature in steps of 1 °C.

This is also seen in the refinement of the isotropic displacement parameter. In the tetragonal phase all displacement parameters increase with temperature as the thermal vibration increases. In the region of the phase transition the two parameters for the different cation positions, which are clearly different in the tetragonal phase, approach each other, and in the cubic phase copper and indium have the same isotropic displacement parameter.

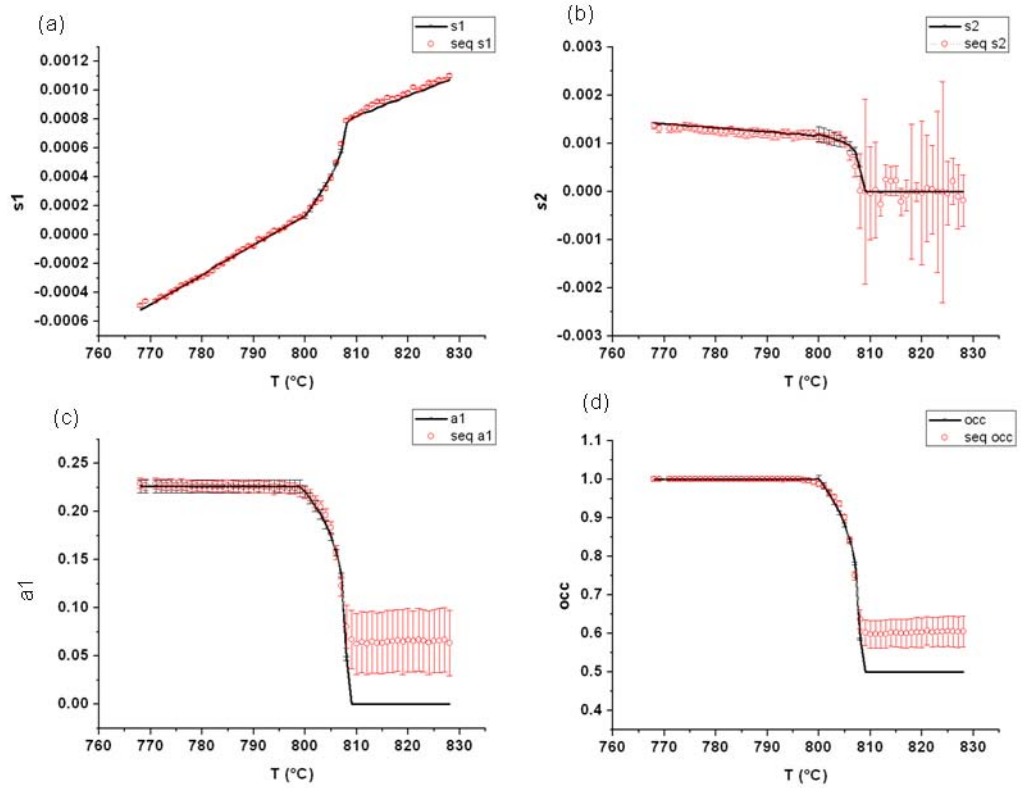

Figure 2: Comparison of values obtained in the parametric (black line) and sequential (red circles) Rietveld refinements. (a) Values obtained for *s1* show very good agreement for the whole temperature range. (b) Values for s2 parameter and respective esd's (c) the a1 parameter shows good agreement in the low temperature and transition region (d) Values for the occupancy of Wyckoff position 4a ($I\bar{4}2d$) with copper.

According to the symmetry mode decomposition with ISODISTORT the primary order parameter of this transition is the W1 mode, which is responsible for the changes in the atomic position of selenium. The critical exponent β obtained in the modelling of this mode ($a1$) gives a value of

0.24(1). This indicates a tricritical displacive phase transition. The isothermal strain *s1* is related to the primary order parameter in this manner: Q*s1* ~ Q*a1*² as expected for the spontaneous strain in co-elastic phase transitions. The critical exponent obtained in parametric Rietveld refinement is 0.49(2). These behaviours are also reflected in the isotropic displacement parameter.

For the two remaining parameters occupancy *occ* and strain *s2* critical exponents of 0.28(1) and 0.16(5) respectively are observed. Values lower than 0.25 can be obtained for dynamic order-disorder transitions or for first-order transitions, while a critical exponent of about 0.3 indicates a three-dimensional ordering phenomenon according to the Ising model.

So, the present phase transition combines an order-disorder and a displacive transition as stated before by Schorr and Geandier (2006) [1]. A comparison of the results obtained in the present study with the results previously obtained by Schorr and Geandier shows that in all cases the power law exponents are in agreement within the esd's.

Assuming the validity of the underlying model, parametric Rietveld refinement can offer a more detailed understanding of the analyzed system. The implementation of equations to describe the evolution of parameters, as shown for the symmetry modes in the present work, reduces the estimated standard deviations leading to more reliable results even in case of lower quality diffraction data.

References:

[1] *Schorr, S. and G. Geandier.* Journal of Crystal Research and Technology 41, 450–457 (2006).

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