

## Lab Report SC-XRD 46

# Higher Dimensional Crystallography: Treatment of Composite Crystals Using Four Dimensions in Space

**Imagine a structure with space group symmetry that has channels in which another compound is found with its own space group symmetry, which is different from the one of the first structure. Both substructures are not stable as such; they obtain their stability from the interaction between them, which causes a modulation of the constituting components. As a result, the atoms of subsystem 1 will undergo a modulation with a periodicity of subsystem 2, and vice versa<sup>1,2</sup>.**

This hypothetical example describes an inter-growth compound, or composite. In comparison to conventional crystals, with a fully periodic three-dimensional arrangement of their building units, composite crystals need an entirely different approach for structure determination. This holds for diffraction data processing, structure solution and refinement, but also for the analysis of the final results. All these steps can be treated skillfully within the higher-dimensional superspace approach.

The structure of  $\text{Rb}_{15}\text{Mn}_{11}\text{O}_{22}$  can be described as a composite structure built up by a honeycomb-like framework of rubidium ions as one subsystem, and by a second subsystem of chains consisting of edge-sharing  $\text{MnO}_4$  tetrahedra (Figure 1). In this case, both substructures have two

common lattice parameters ( $a, b$ ) but different translation symmetry along the third direction ( $c_1, c_2$ )<sup>3</sup>.

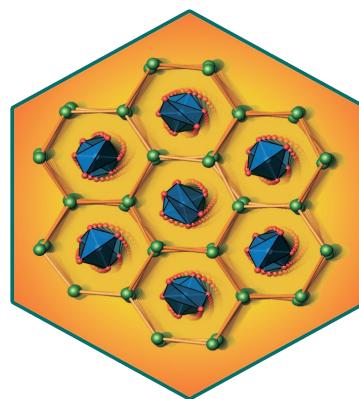


Figure 1:  $\text{Rb}_{15}\text{Mn}_{11}\text{O}_{22}$  Composite Structure

## Data Collection

Measurements were done on a SMART APEX II diffractometer, using Mo-K $\alpha$  radiation. At room temperature a complete sphere was collected using 0.3 degree scans, 30 seconds exposure time, and a detector distance of 60 mm.

## Four Indices for Four Dimensions

Indexing of the diffraction data is already a big challenge, because all auto-indexing procedures usually fail. For  $\text{Rb}_{15}\text{Mn}_{11}\text{O}_{22}$ , these routines can only find a supercell with an exceptional long c-axis of  $\sim 60 \text{ \AA}$  (Figure 2). For a careful inspection of the reciprocal space the Pseudo Precession photograph module of Bruker's APEX2 software package<sup>4</sup> is used. This tool allows a detailed exploration of the recipro-

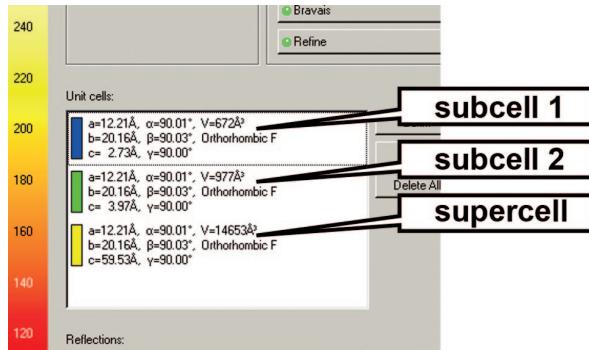


Figure 2: Unit cells after manual investigation

cal space (Figure 3) without being restricted to integer  $hkl$  values. Indeed, most of the allowed reflections are missing and the strongest diffraction intensities can be indexed by using two sets of indices  $hkl$  (or better  $hk\bar{l}0$ ) and  $hkm$  (or better  $hk0m$ ), which correspond to two subcells with different c-axes. The data can be combined to one dataset by the use of four indices ( $hklm$ ), meaning four dimensions in space, whereby reflections

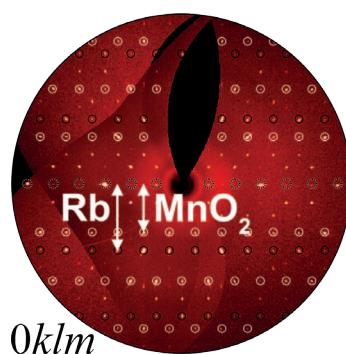


Figure 3: Precession Image

of subcell 2 are addressed as satellites of subcell 1, and vice versa. It should be pointed out, that composites are a special case of modulated structures. In the latter case the index  $m$  addresses the satellites of the main reflections ( $hkl$ ). In composites, however, the index  $m$  addresses the satellites of subset 1 ( $hkl$ ) and index  $/$  addresses the satellites of subset 2 ( $hkm$ ).

Weak peaks are satellite reflections ( $hklm$  with  $/$  and  $m > 0$ ) caused by the interaction between the two subsystems. The  $n^{\text{th}}$  order of satellite reflections is not given by  $m$ , exclusively;

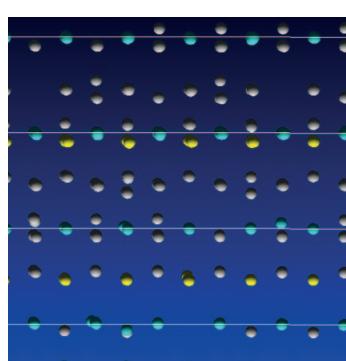


Figure 4: Peak Selection with RLatt

is defined as **either / or**  $m \leq n$ . Here, with  $n = 1$ , mostly all diffraction data with visible intensities can be indexed, and the "empty" reciprocal space is left unindexed.

The peak selection and indexing can be done manually with the help of Bruker's RLatt<sup>4</sup> (Figure 4), resulting in the correct unit cells parameters (Figure 2) of the Rb- and  $\text{MnO}_2$ -subsystems.

## Integration

Bruker's integration engine SAINT<sup>4</sup>, allows processing of the diffraction data via two different ways:

- Use of a 3D supercell ( $a, b, c$ ) for integration, this can be regarded as the lowest common multiple of the two subcells. Absorption correction follows by using SADABS<sup>5</sup>. To obtain an  $hklm$  dataset, the three-dimensional data have to be re-indexed with respect to the lattice constants and modulation wave vector of one of the subsystems (in this case  $a_1^*, b_1^*, c_1^*, q_1$ ). Calculations were performed using JANA2006<sup>6</sup>. This approach requires a commensurate structure, or at least an approximation on it.
- For integration of the data use the lattice parameters of one subsystem (e.g.  $a_1, b_1, c_1$ ) and add a modulation wave vector, which is given by the lattice parameters of the other subsystem (in this case  $q = c_1/c_2$ ) for integration. In contrast to approach a) this one is more general since it also works for incommensurate cases. Conveniently, a  $hklm$  dataset results directly from SAINT, which in a next step is corrected for absorption with SADABS.

## Structure Solution and Refinement

In the case of  $\text{Rb}_{15}\text{Mn}_{11}\text{O}_{22}$ , a starting model for the basis structure can be derived from the superstructure in three-dimensional space. If this is not possible the program SUPERFLIP<sup>7</sup> can be used, a program for the solution of crystal structures by charge flipping in arbitrary dimensions. The refinement procedure, using JANA2006, starts with developing the superspace model for the crystal structure by refinement of the basic structure against the main reflections, followed by subsequent introduction of modulation parameters and refinement against the complete dataset including satellite reflections. In this case, it was necessary to use up to six-order harmonic coefficients of the modulation functions (Figure 5).

## Results

The composite structure of  $\text{Rb}_{15}\text{Mn}_{11}\text{O}_{22}$  cannot be described in three dimensions without difficulties. However, it is highly symmetrical in four dimensions, only three atomic sites are needed (one for each Rb, Mn, and O atom), instead of 31 using a 3D superstructure as model. The 4D dataset ( $hklm$ ) can be indexed with four lattice constants ( $a$ ,  $b$ ,  $c_1$ ,  $c_2$ ). This dataset contains the information of both subsystems ( $hkl0$  and  $hk0m$ ) and the interaction between them ( $hklm$ ). The structural properties: bond distances, angles, coordination environments, and charges of the involved atoms can only be reflected and analyzed correctly by using the superspace approach (Figure 6).

## Refinement Results (JANA2006)

Chemical formula:  $\text{Rb}_{15}\text{Mn}_{11}\text{O}_{22}$  ( $\text{Mn}_{0.733}\text{O}_{1.467}\text{Rb}$ )  
Crystal system, space group: orthorhombic,  $Fddd(00\gamma)ss0$

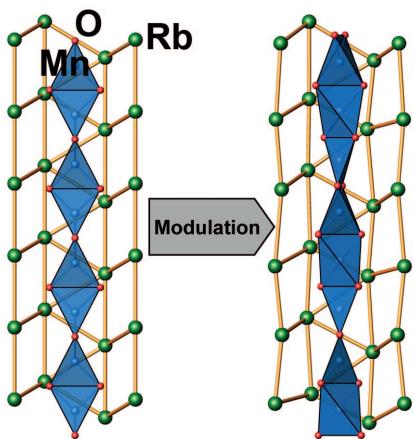


Figure 5: Solve and Refine

### Subsystem 1: Rb

$a_1 = 12.1639(4)$  Å,  $b_1 = 20.1013(7)$  Å,  $c_1 = 3.9865(2)$  Å  
Modulation wave vector  $q_1 = 0 0 15/22 (0.68182)$

### Subsystem 2: $\text{MnO}_2$

$a_2 = a_1$ ,  $b_2 = b_1$ ,  $c_2 = 2.7181(2)$  Å  
Modulation wave vector  $q_2 = 0 0 22/15 (1.46667)$

### 3D Supercell

Crystal system, space group: orthorhombic,  $Fddd$   
 $a = a_1$ ,  $b = b_1$ ,  $c = 15 \times c_1 = 22 \times c_2 = 59.798(2)$  Å

$R[F^2 > 2\sigma(F^2)]$ ,  $wR(F^2)$ ,  $S$ : 0.041, 0.059, 1.17

## Conclusion

- Visual representation and graphical tools of APEX2 for peak selection are essential to successfully index composite crystals as well as other modulated structures.
- Data integration can be performed for modulated structures using SAINT.
- Absorption correction and scaling for modulated structures can be applied using SADABS.
- Solving, refinement, and analyzing of modulated structures can be performed with JANA2006<sup>6</sup>.

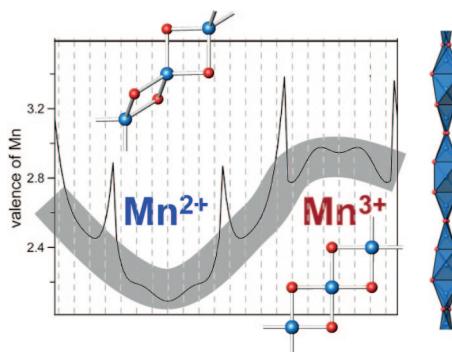


Figure 6: Analyze Structure

## References

- 1 Janssen, T.; Chapuis, G.; Boissieu, M. de (2007). Aperiodic Crystals, Oxford University Press, Oxford, UK.
- 2 Smaalen, S. van (2007). Incommensurate Crystallography, Oxford University Press, Oxford, UK.
- 3 Nuss, J.; Pfeiffer, S.; Smaalen, S. van; Jansen, M. (2010). Acta Crystallogr. B66, 27-33.
- 4 Bruker (2011). APEX2, Bruker AXS, Madison, USA.
- 5 Sheldrick, G. M. (2008). SADABS, Bruker AXS, Madison, USA.
- 6 Petricek, V.; Dusek, M.; Palatinus, L. (2006). JANA2006, Institute of Physics, Praha, Czech Republic.
- 7 Palatinus, L.; Chapuis, G. (2007). SUPERFLIP, J. Appl. Cryst. 40, 786-790.

## Author

Jürgen Nuss  
Max Planck Institute for Solid State Research, Heisenbergstraße 1,  
70569 Stuttgart, Germany



### Bruker AXS GmbH

Karlsruhe · Germany  
Phone +49 721 50997-0  
Fax +49 721 50997-5654  
[info@bruker-axs.de](mailto:info@bruker-axs.de)

[www.bruker.com](http://www.bruker.com)

### Bruker AXS Inc.

Madison, WI · USA  
Phone +1 800 234-XRAY  
Phone +1 608 276-3000  
Fax +1 608 276-3006  
[info@bruker-axs.com](mailto:info@bruker-axs.com)