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User Manual

Unit-cell determination of crystalline phases

in TEM experiments

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1. Introduction

Determining the unit cells of unknown crystalline phases is a fundamental requirement for materials characterization and the initial step in ab initio structure determination. Electron diffraction, alongside X-ray and neutron diffraction techniques, has been extensively used in material characterization and crystal structure determination. Lattice parameters obtained from selected-area electron diffraction (SAED) have an accuracy of approximately 5%.

A SAED pattern can be viewed as a two-dimensional section of a three-dimensional reciprocal lattice. By using a double tilt holder in a transmission electron microscope (TEM), a series of reciprocal planes can be obtained. Due to the nature of the SAED technique, it is logical to determine the unit cell of an unknown crystalline phase from a tilt series of electron diffraction patterns. This traditional method, documented by Vanishtein (1964) and Zou *et al*. (2011), is, however, cumbersome when applied to crystalline phases in monoclinic or triclinic systems.

A crystalline lattice can be uniquely characterized by a reduced cell, and there are 44 primitive Niggli reduced cells corresponding to 14 Bravais lattices (Niggli, 1928). The Niggli cell is crucial due to its uniqueness and its use in determining the Bravais type of the lattice (Gruber, 1973). The Niggli cell has been widely used in X-ray crystallography (e.g., Santoro and Mighell, 1970) and in electron diffraction experiments for unit-cell determination of crystalline phases (Kuo, 1978). A modified cell reduction method was adopted in the early version of this software (Li, 2005) and later by Zhao *et al*. (2008). Recently, Yang *et al*. (2017) described a cell reduction approach for unit-cell determination from three specially related SAED patterns, allowing accurate calculation of the angles between each pair of patterns.

A general 3D reciprocal lattice reconstruction method was discussed by Fraundorf (1981), and a program with a visual 3D reciprocal space for this purpose was developed by Zou *et al*. (2004). Jiang *et al*. (2009, 2011) developed an algorithm for unit-cell determination of crystalline phases from a collection of randomly oriented SAED patterns. The electron diffraction tomography technique (Kolb *et al*., 2007, 2008) and the diffraction rotation technique (Zou *et al*., 2011) have also garnered significant interest. The diffraction rotation technique aims to collect a complete data set of diffraction patterns in a fashion like X-ray crystallography.

We developed a set of computer programs for the determination of unit-cell in electron diffraction experiments (Li, 2005), including a modified cell reduction method. The program set has been greatly updated for improvement. The current version is described in this manual, which is a practical tool for the determination of the unit cell of the crystalline phase in TEM, including 1) reciprocal lattice reconstruction approach, 2) the cell reduction approach, and 3) the lattice refinement.

We developed a set of computer programs for unit-cell determination in electron diffraction experiments (Li, 2005), including a modified cell reduction method. This program set has been significantly updated for improvement. The current version, described in this manual, serves as a practical tool for unit-cell determination of crystalline phases in TEM, encompassing: 1). Reciprocal lattice reconstruction approach, 2). Cell reduction approach, and 3). Lattice refinement.

2. Theory background

In the method described, unit-cell determination of crystalline phases relies on a tilt series of selected-area electron diffraction (SAED) patterns, where each pair shares a common reflection vector. A reflection vector is defined as the vector from the incident beam to a reflection spot on the diffraction pattern. The reconstruction of a reciprocal lattice from a tilt series of SAED patterns is straightforward. Assuming there is one reflection vector on each SAED pattern perpendicular to the common reflection vector in a tilt series, a 2D lattice can be reconstructed based on these reflection vectors and their tilt angles. A 3D lattice is then obtained by the combination of the 2D lattice and the common reflection vector. In SAED experiments, it is usually to select the shortest reflection vector among all the observed reflections to be the common reflection vector in a tilt series of SAED patterns for unit-cell determination. The basic procedures for unit-cell determination of crystalline phases using SAED data are (i) a reciprocal lattice (or primitive cell), (ii) a direct lattice (or primitive cell), (iii) a cell reduction if necessary, and (iv) a refinement of lattice parameters.

The concept of Niggli-cell-reduction theory, originally applied in X-ray crystallography, was later extended to electron diffraction experiments. In 1928, Niggli demonstrated that a crystal lattice could be uniquely characterized by a reduced cell, yielding 44 primitive Niggli reduced cells corresponding to the 14 Bravais lattices (Niggli, 1928). The significance of the Niggli cell lies in its ability to determine the Bravais type of the lattice due to its unique representation (Gruber, 1973). There are two steps in the determination of the unit-cell: the determination of a reduced direct primitive cell and the transformation to a conventional cell. Clegg (1981) proposed a procedure to overcome the problem by directly comparing the reduced cell to 44 forms of the Niggli cell. Following the identification of the appropriate Niggli cell, a least-squares refinement procedure is often employed to generate refined lattice parameters. This refinement process ensures that the lattice parameters accurately reflect the structural characteristics observed in the diffraction patterns.

A flow chart of the Niggli cell reduction procedures in TEMUC3 is shown in Figure 1. In the first step, a primitive cell can be generated in two methods, either (i) from two SAED patterns with a common vector and a tilt angle between them (Li 2005) or (ii) from three SAED patterns with a common reflection vector among each pair of the patterns (Yang *et al*., 2017). Figure 2 shows the geometry to generate a primitive cell from two SAED diffraction patterns. Assuming three vectors, a^*, b^*, c^*, span a primitive cell, where a^* and b^*, span the plane-1 and a^* and c^* span the plane-2. The angle between plane-1 and plane-2 is ϕ. Thus, the angles of the primitive cell are $\alpha^* = \angle COQ$ (or $\angle POB$), $\beta^* = \angle TOQ$ (ω_1), $\gamma^* = \angle TOC$ (ω_2). The geometry to deduce a primitive cell from three SAED patterns was described in the published paper by Yang *et al*. (2017).

The second step is to transform the primitive cell from reciprocal space to direct space. The third step is to make a cell reduction. An algorithm developed by Krivy and Gruber (1976) was used in TEMUC3. The fourth step is to convert from a Niggli cell to a conventional unit-cell. The procedure proposed by Clegg (1981) was used in TEMUC3. This procedure overcomes the problem by directly comparing the reduced cell to 44 forms of the Niggli cell. The final step is to index the SAED patterns and then to refine the lattice parameters. A general algorithm of least-squares refinement was described in the previous paper (Li, 2005). For application, the refinement of lattice parameters is better to carry out for seven crystal system separately. The data set of reflection vectors are indexed within error tolerance and then the lattice parameters can be refined using the lengths of reflection vectors.

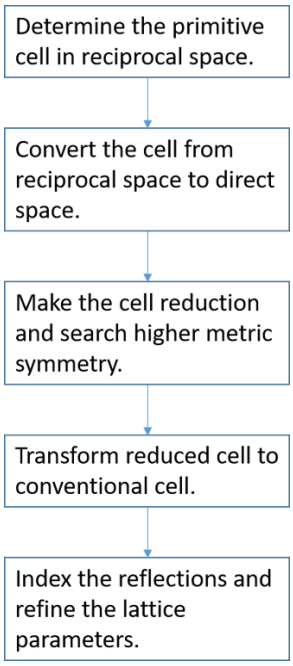

Figure 1. A flow chart of the Niggli cell reduction procedure in TEMUC3.

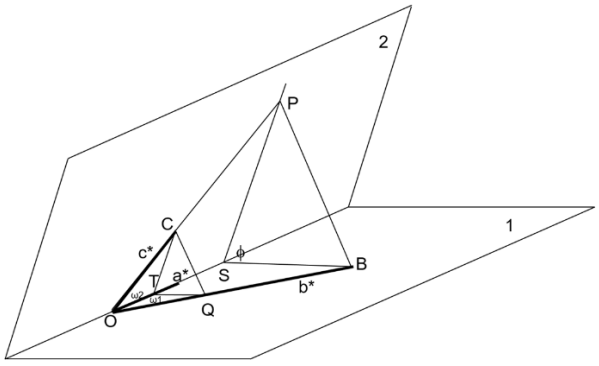

Figure 2. Geometry for generating a primitive cell from two SAED diffraction patterns and the angle between them. Plane-1 and plane-2 are the two SAED patterns and the angle between them is φ. A primitive cell is defined by a*, b*, c* and α* = ∠ COQ (or ∠ POB), β* = ∠ TOQ (ω1), γ*= ∠ TOC (ω2).

3. Design of TEMUC

TEMUC provides tools for (i) a conventional lattice reconstruction, (ii) unit cell determination with cell reduction, and (iii) lattice parameter refinement. The tools can be activated with a dropdown menu or the menu bar and used in various orders according to the task.

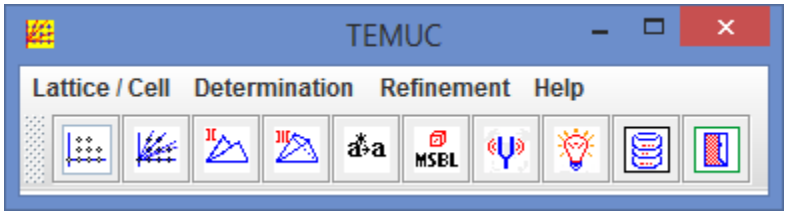

Figure 3. The menu of the TEMUC software.

The normal procedure for Bravais lattice/unit cell determination is (i) reciprocal lattice/cell, (ii) direct lattice/cell, (iii) cell reduction, if necessary, (iv) lattice/cell refinement. The dialogs for the reciprocal lattice reconstruction are shown in Figure 4. The experimental data of the SAED patterns can be inputted in the Reciprocal Lattice Data dialog and displayed in the TEMUC panel. The data analysis is carried out via the Reconstruction dialog. The experimental data can be saved and reloaded.

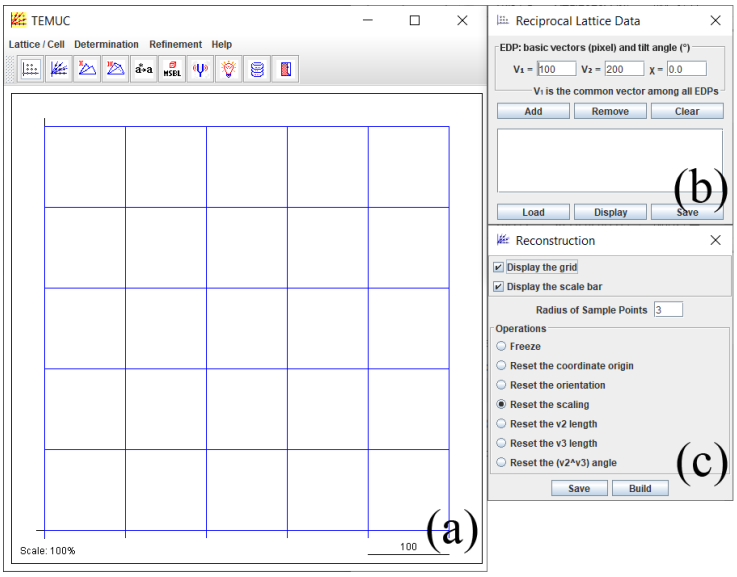

Figure 4. The GUI of the conventional method in the TEMUC software.

Two dialogs for building the reciprocal cells to be reduced are shown in Figure 5. One is for the cell built from two SAED patterns plus the tilt angle between them (Li 2005), and the other is for the cell built from three the SAED patterns, in which each pair shares a common reflection/vector (Yang *et al*. 2017).

Figure 6 shows the dialog for the conversion from reciprocal lattice/unit cell to direct lattice/unit cell and the dialog for a cell reduction / Bravais lattice (metric lattice). Figure 7 shows the dialog for lattice refinement from the experimental data of the SAED patterns. The experimental data can be saved and reloaded.

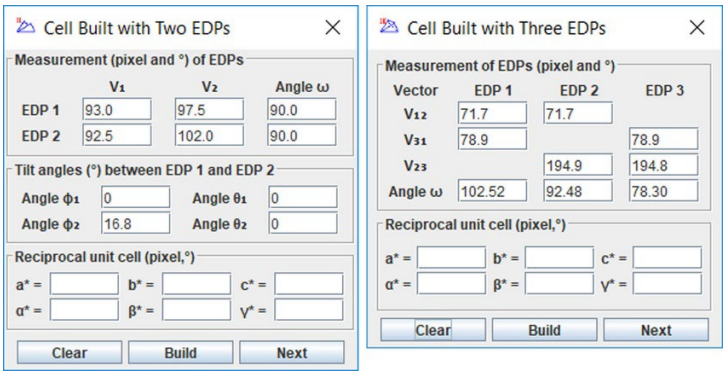

Figure 5. The GUI of the reduced-cell methods in the TEMUC software.

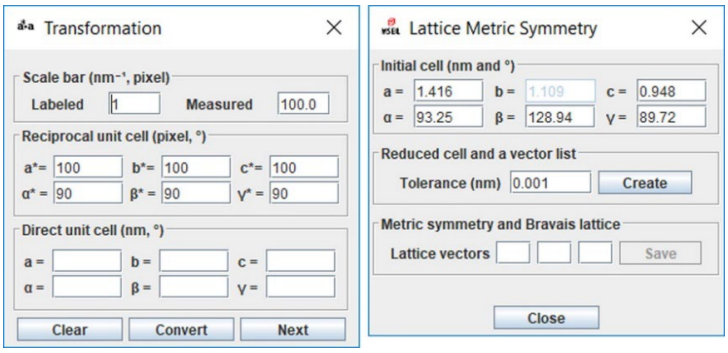

Figure 6. The GUI of the transformation method in the TEMUC software.

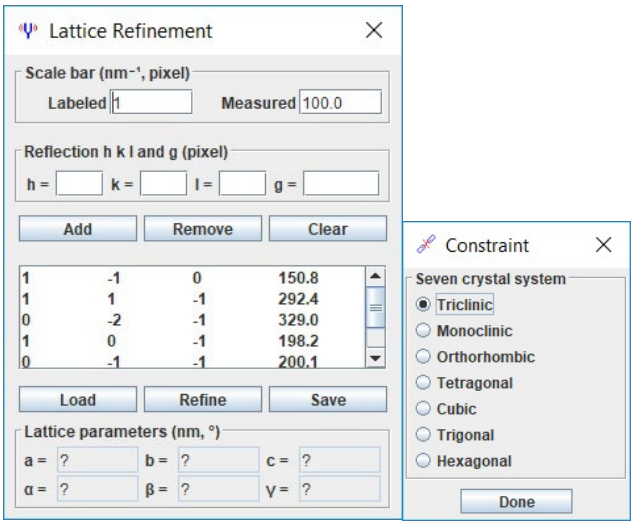

Figure 7. The GUI of the lattice refinement method in the TEMUC software.

4. Usage of TEMUC

4. 1 A conventional method of the lattice reconstruction

The reciprocal length of reflection/vector and the angle between two vectors can be precisely measured with QSAED software.

Vector 1 should be inputted as the common vector and vector 2 as the other vector; the angle χ is the tilt angles for the SAED patterns. The data set can be saved to a file and reloaded for a demo in a classroom. A demo data can also be loaded by clicking the light bulb icon in the menu bar.

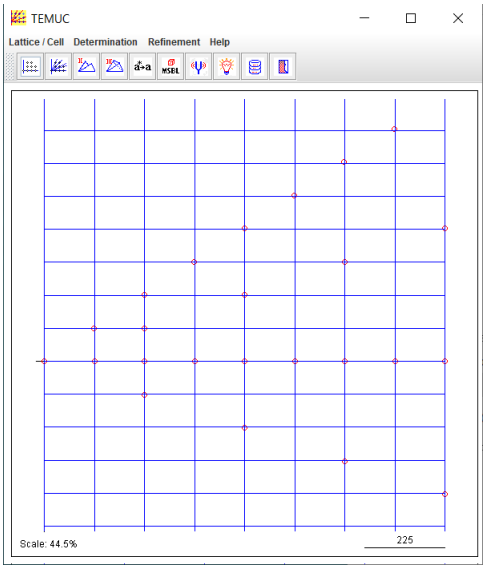

Figure 8. The application of the convention method in the TEMUC software.

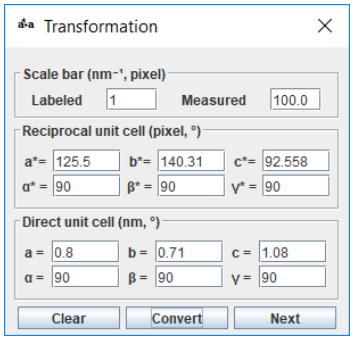

Figure 9. The application of the transformation method in the TEMUC software.

When the data is ready, the graphics of the data will be displayed in the panel by clicking the Display button. Adjust the net with each operation to match the experimental data; for example, the demo data in Figure 8. Rotate the data set to make the short vector parallel to the horizontal axis.

When the net is matched with experimental data, the reciprocal/direct unit cell can be built, as shown in Figure 9.

4.2 Cell reduction method of unit cell determination

Cell reduction method is (i) to get the cell from the experimental data; (ii) to get the Niggli cell by reduction; (iii) to transfer the Niggli cell to Bravais lattice/unit cell.

Figure 8 shows a method to get the cell from two SAED patterns (Li, 2015) and a method to get the cell from three SAED patterns (Yang *et al*. 2017). In the first method, vector 1 should be inputted as the common vector and vector 2 as the other vector. Unlike the two reflections/vectors in a SAED pattern used in the conventional method, the angle ω is not restricted to be 90º. In the second method, the common vectors in SAED patterns are marked. It is worthy of pointing out that the derived cell should be the smallest one in the reciprocal space. Here is the two-dimensional analog in Figure 9. The cells spanned by V_1 and V_2 or V_1 and V_3 or V_1 and V_4 or V_2 and V_3 are the smallest cells. On the other hand, the cells spanned by V_2 and V_4 or V_3 and V_4 are not the smallest cells.

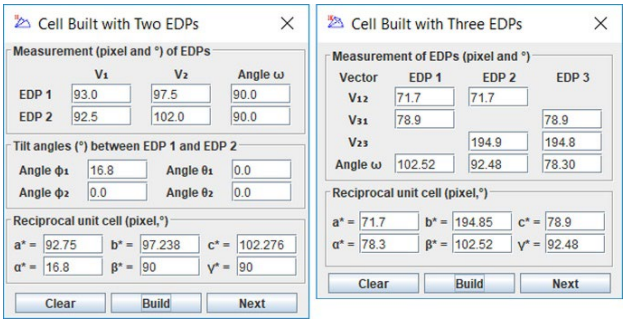

Figure 8. The application of the reduced-cell method in the TEMUC software.

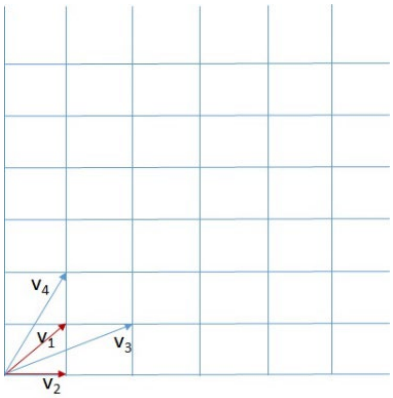

Figure 9. The two-dimensional analogy for the reduced cell.

Cell reduction and metric symmetry will be made in Figure 6. The algorithm proposed by Clegg (1981) was used in the tool. The reduced cell parameters and the vector list will be saved

to a file. If there are higher metric symmetry (angle between two vectors is near 90º), the labels of the vectors related to the higher metric symmetry can be inputted the lattice vector, the possible Bravais lattice/unit cell can be saved in a file.

4.3 Unit cell refinement

The parameters of the unit cell should be refined if a list of reflections is available. Each reflection with its spacing measured in the experiment can be indexed by using the lattice parameters determined in previous work. The data set can be saved to a file, and then reloaded for the demonstration in a classroom. A constraint for the refinement needs to be selected, and then the final refined lattice parameters can be obtained.

5. Installation and license

TEMUC can be used as a stand-alone computer program or as one component in the Landyne software suite. The Landyne suite are available in

https://www.unl.edu/ncmn-enif/xzli/computer-programs
https://landyne.com

Decompress the compressed files to a specified fold e.g., c:\landyne6\. Make sure the latest Java Runtime Environment (e.g. openJDK21) has been installed on the computer (PC) beforehand. Double click the .exe file to start the software.

A license is available from Landyne (jlandyne@gmail.com). Without the license, the software can be used in a demo mode. The sample data can be loaded from the light-bulb icon in the menu bar.

6. References

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