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Accurate determination of lattice parameters based on Niggli reduced cell theory by using digitized electron diffraction micrograph

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ABSTRACT

In this paper, we used Niggli reduced cell theory to determine lattice constants of a micro/nano crystal by using electron diffraction patterns. The Niggli reduced cell method enhanced the accuracy of lattice constant measurement obviously, because the lengths and the angles of lattice vectors of a primitive cell can be measured directly on the electron micrographs instead of a double tilt holder. With the aid of digitized algorithm and least square optimization by using three digitized micrographs, a valid reciprocal Niggli reduced cell number can be obtained. Thus a reciprocal and real Bravais lattices are acquired. The results of three examples, i.e., Mg_4Zn_7, an unknown phase (Precipitate phase in nickel-base superalloy) and $Ba_4Ti_{13}O_{30}$ showed that the maximum errors are 1.6% for lengths and are 0.3% for angles.

1. Introduction

Using electron diffraction technique, it is easy to obtain single-crystal electron diffraction patterns of individual micro/nano-sized crystals in transmission electron microscopes (TEM) (Li, 2005; Zhang, 2010). There is an increasing need for accurate lattice parameter determination by electron diffraction method because it is difficult to collect diffraction data with a micro/nano crystal by X-Ray diffraction (XRD). However, the accuracy for determining lattice constants by XRD is much better than that by electron diffraction method due to the inaccuracy of measuring rotation angles by a double tilt holder in an electron microscope. The crucial challenge is to overcome this problem.

In the past, many researchers, for example, Zou et al. (2004), Li (2005) made a great deal of effort to improve the accuracy of measuring lattice constants including using digitized micrograph to determine peak position instead of by fine glass rule measurement, and using the least square method to further optimize parameters and calibrate rotation angle etc. These measurements can eliminate a part of error arising from the error of measuring the rotation angle; however, these methods are not sufficiently effective.

In this paper, we used Niggli reduced cell theory to measure the angle between two reciprocal lines directly on the micrograph instead of using a double tilt holder.

A Niggli reduced cell corresponds to a unique Bravais lattice, and a minor error might cause a big problem in determining which Niggli number is correct among the 44 ones, meaning that the parameters for determining the Niggli number should be very accurate. To solve this problem, we used the digitized micrograph to determine the peak of each electron diffraction spot and then used the least square method to optimize parameters.

2. Theory of the method

2.1. The foundation of the Niggli reduced cell

A selected area election diffraction (SAED) pattern is a two dimensional section of a three dimensional reciprocal lattice. According to this phenomenon, a series of the reciprocal plane can be obtained by rotating a double tilt holder, hence the whole reciprocal lattice can be constructed (Tilley, 2006).

Any two different reciprocal planes should have an intersecting reciprocal lattice line, therefore three reciprocal planes located at the two different reciprocal zone axes should have three intersecting reciprocal lattice lines. If these three reciprocal planes are located at a single reciprocal zone axis, there is only one intersecting reciprocal lattice line. If three electron diffraction patterns A, B and C located at the three different reciprocal zone axes, there should exist three intersecting reciprocal lattice lines as shown in Fig. 1, where $\mathbf{B}_1^*$, $\mathbf{B}_2^*$ and $\mathbf{B}_3^*$ are their intersecting reciprocal lattice lines, and α_1^*, α_2^*, and α_3^* are the angles between $\mathbf{B}_2^*$ and $\mathbf{B}_3^*$, $\mathbf{B}_1^*$ and $\mathbf{B}_3^*$, $\mathbf{B}_1^*$ and $\mathbf{B}_2^*$, respectively. It can be found from Fig. 1 that the angles α_1^*, α_2^* and α_3^* can be measured directly on the electron diffraction

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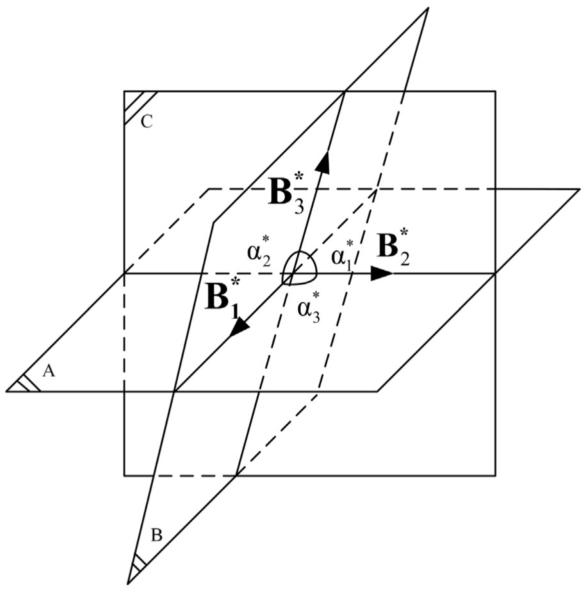

Fig. 1. The schematic plot of three-dimensional reconstruction. A, B and C are the three electron diffraction patterns ($\mathbf{B}_1^*$, $\mathbf{B}_2^*$ and $\mathbf{B}_3^*$ are the intersecting reciprocal lattice lines and α_1^*, α_2^* and α_3^* are the angles among $\mathbf{B}_1^*$, $\mathbf{B}_2^*$ and $\mathbf{B}_3^*$).

pattern C, B and A respectively and the lengths of $\mathbf{B}_1^*$, $\mathbf{B}_2^*$ and $\mathbf{B}_3^*$ can be measured on the A, B and C as well. Hence the lengths of $\mathbf{B}_1^*$, $\mathbf{B}_2^*$, $\mathbf{B}_3^*$ and the angles of α_1^*, α_2^*, and α_3^* can be measured very accurately because the peak position of each electron diffraction spot can be determined by digitization method and optimized peak positions by least square method. The accuracy of angles α_1^*, α_2^* and α_3^* can be reached to 0.1–0.2°. If the indexes (u_1, v_1, w_1), (u_2, v_2, w_2), and (u_3, v_3, w_3) of the three reciprocal planes A, B and C form a primary unit-cell, their intersecting reciprocal lattice lines of $\mathbf{B}_1^*$, $\mathbf{B}_2^*$ and $\mathbf{B}_3^*$ will form a primary reciprocal cell as well. Once an accurate primary cell is obtained, one may reduce it to a standard Niggli reduced cell, and then a reciprocal Niggli reduced cell number is obtained. Thus lattice constants of the reciprocal Bravais lattice are determined, finally, the lattice constants of a real-space Bravais lattice are determined by matrix transformation.

For convenience of readers, we introduce the Niggli reduced cell theory briefly as follows:

In 1928, Niggli proved that a crystal lattice can be characterized by a unique choice of a reduced cell and there are 44 primitive Niggli reduced cells corresponding to the 14 Bravais cells (Niggli, 1928). The importance of the Niggli cell is due to its uniqueness and the possibility that it can be used for determining the Bravais type of the lattice (Gruber, 1973).

If we have lattice constants of a reduced cell $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, α^*, β^*, γ^* in the right-handed coordinate system, a metric matrix

$$\mathbf{G} = \begin{pmatrix} \mathbf{a}^*\cdot\mathbf{a}^* & \mathbf{b}^*\cdot\mathbf{b}^* & \mathbf{c}^*\cdot\mathbf{c}^* \\ \mathbf{b}^*\cdot\mathbf{c}^* & \mathbf{a}^*\cdot\mathbf{c}^* & \mathbf{a}^*\cdot\mathbf{b}^* \end{pmatrix} = \begin{pmatrix} S_{11} & S_{22} & S_{33} \\ S_{23} & S_{13} & S_{12} \end{pmatrix}, \quad (1)$$

where the three interaxial angles should be either all acute or all obtuse (Azaíroff and Buerger, 1958). This rule confirms that S_{ij} are all positive (Type I cell) or all negative (Type II cell). If one or more of the S_{ij} is zero, the cell will be considered to be of Type II.

The cell represented by the metric matrix **G** is a standard Niggli reduced cell, only if the following conditions are satisfied (Niggli, 1928).

(A) Positive reduced cell form, Type I cell, all the angles <90°. Main conditions:

$$S_{11} \le S_{22} \le S_{33};\, S_{23} \le \frac{1}{2}S_{22};\, S_{13} \le \frac{1}{2}S_{11};\, S_{12} \le \frac{1}{2}S_{11}.$$

Special conditions:

(a)If $S_{11} = S_{22}$ then $S_{23} \le S_{13}$;

If $S_{22} = S_{33}$ $S_{13} \le S_{12}$.

(b)if$S_{23} = \frac{1}{2}S_{22}$then$S_{12} \le 2S_{13}$;

if$S_{13} = \frac{1}{2}S_{11}S_{12} \le 2S_{23}$;

if$S_{12} = \frac{1}{2}S_{11}S_{13} \le 2S_{23}$.

(B) Negative reduced form, Type II cell, all angles ≥ 90°. Main conditions:

$$S_{11} \le S_{22} \le S_{33};\, |S_{23}| \le \frac{1}{2}|S_{22}|;\, |S_{13}| \le \frac{1}{2}|S_{11}|;\, |S_{12}| \le \frac{1}{2}|S_{11}|;\, (|S_{23}| + |S_{13}| + |S_{12}|) \le \frac{1}{2}(S_{11}+S_{22})$$

Special conditions:

(a)if$S_{11} = S_{22}$ then $|S_{23}| \le |S_{13}|$;

if $S_{22} = S_{33}$ $|S_{13}| \le |S_{12}|$.

(b) if $|S_{23}| = \frac{1}{2}S_{22}$ then $S_{12} = 0$;

if $|S_{13}| = \frac{1}{2}S_{11}\, S_{12} = 0$;

if $|S_{12}| = \frac{1}{2}S_{11}\, S_{13} = 0$;

if $(|S_{23}|+|S_{13}|+|S_{12}|) = \frac{1}{2}(S_{11}+S_{22})$ then $S_{11} \le 2|S_{13}| + |S_{12}|$.

The main conditions define a cell based on the shortest three non-coplanar vectors. Conditions (a) break down ambiguity when two cell edges are equal, and conditions (b) define the Niggli cell when there is more than one symmetrically independent cell based on the shortest three non-coplanar vectors (Krivy and Gruber, 1976; Santoro and Mighell, 1970).

The core idea of this method is the determination of a Niggli reduced cell and the transformation of it to a conventional Bravais cell. Kuo (Kuo, 1978; Kuo et al., 1983) applied the concept of the Niggli reduced cell and cell reduction technique on the unit-cell determination in electron diffraction experiments. But Kuo's method is laborious due to its direct comparison between the 44 Niggli cells and the corresponding 14 Bravais lattices.

A unit-cell characterized by the three shortest non-coplanar translations is not reduced if it fails to satisfy one of the special conditions. In this case, the cell must be transformed to obtain the reduced cell; however, the matrices were provided by Santoro and Mighell (1970). Some reviews on the Niggli cell and its applications can be consulted in literature (e.g., (Andrews and Bernstein, 2014; Himes and Mighell, 1982a,b; Jiang et al., 2009; Mighell and Rodgers, 1980; Zhao et al., 2008; Zou et al., 2004; Zuo et al., 1995)).

2.2. Procedure for reconstruction of lattice constants by ED patterns

2.2.1. Determining peak positions of ED patterns by digitization method

Three electron diffraction patterns are chosen for lattice constant reconstruction first (See Figs. 4 a–c; 5 a–c and 6 a–c), then the positions of all the diffraction spots on each SAED pattern and