Simulation and Analysis of Electron Diffraction and CBED Patterns

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ABSTRACT

About 10 samples have been simulated, including their crystal structures, diffraction patterns and convergent beam electronic diffraction (CBED) patterns under different conditions, such as voltage, sample thickness and Gmax (maximum value of scattering vector). Then, crystal structure parameters and other relevant information have been read from the patterns and calculation results. Crystal structures of all samples have been simulated to conduct further simulation. Diffraction patterns of several different sulphides have been simulated to study the structure difference among them. The major part of this project is the simulation of CBED patterns of Kieserite ($\text{Cu}_2\text{ZnSnS}_4$) and the Cubic ZnS. Analysis was done based on these results to demonstrate the application of simulation software of TEM.

INTRODUCTION

TEM was invented in the early 1930s and have been used widely ever since to obtain structural information of materials. CBED is a very powerful method to obtain crystal structural information in TEM. Several software have been developed to simulate TEM images, such as MacTempas which is used for this project. Various functions can be done by simulation, such as CBED patterns. From these patterns, crystal structures, sample thickness, layered structures, 2D and 3D symmetries can be read and can be used in analyses of the symmetry changes, accurate mapping of the distribution of valence electrons in semiconductors, phase identification and strain measurement around precipitates, etc.

SIMULATION METHODOLOGY

The main applications of MacTempas include the calculation of images, diffraction patterns, display of calculated results etc. The input is facilitated through a data-bank of the 230 space groups. Using this software requires basic knowledge of crystallography and additional information based on particular samples.

RESULTS AND ANALYSIS

Structures and Electron Diffraction Patterns of Selected Crystals

Simulation of crystal structure is the first step for simulating diffraction patterns, CBED and other complex patterns. And from diffraction patterns, basic symmetry and structure information like crystal system can be read. Also lattice planes can be allocated based on 7 different crystal systems.

Figure 1 is a combined image for four samples (A,B,C,D). A is Al (cubic structure, space group no.:225); B is CdSe (trigonal structure, space group no. : 143); C is Cubic ZnS (cubic structure,
space group no.:216). And D1, D2 and D3 are Kesterite(Cu₂ZnSnS₄) structures from different angles (tetragonal structure, space group no.:121).

![Crystal structures of four different samples.](image)

Figure 1. Crystal structures of four different samples.

Figure 2 shows diffraction patterns for four different sulphides (S1, S2, S3, and S4). Zone axis are all <0,0,1>. S1 is Cubic ZnS which has symmetry F43m; B is Cu₂ZnSnS₄ (Tetragonal, I42m); C is MoS₂ (Hexagonal, P6₃/mmc) and D is SSn (Orthorhombic, Pnma).

![Diffraction patterns of several sulphides.](image)

Figure 2. Diffraction patterns of several sulphides.

**Kinematic CBED pattern**

TEM has two different modes for CBED, kinematic and dynamic. Kinematic is a simplified mode of which sample thickness is much smaller than the extinction distance. Two kinematic patterns of Cu₂ZnSnS₄ are show in Figure 3. A is under 400 kV voltage and B is under 200 kV.

![Kinematic CBED patterns of Cu₂ZnSnS₄ under different voltage](image)

Figure 3. Kinematic CBED patterns of Cu₂ZnSnS₄ under different voltage
Cu$_2$ZnSnS$_4$ is a very important semiconductor material and it has a tetragonal structure which can be read from Kinematic pattern. Under 400 kV, more spots are calculated than 200kV.

**CBED (dynamic) Pattern Analysis of Two Selected crystals**

CBED is used for crystal samples thicker than one third of the extinction distance (Champness, 2001), so the intensity of diffracted beam is large enough and re-diffraction becomes possible. It allows wide range of illumination angles which is not possible in XRD and it is also used in space-group determination and strain measurement with HOLZ (high order Laue Zone)-line shifts.

CBED calculation is very complex even by simulation software. CBED of two samples were studied, namely, the Cubic phase of ZnS crystal and Kesterite (Cu$_2$ZnSnS$_4$) which is a very important semiconductor material.

In Figure 4, pictures of CBED patterns of Cu$_2$ZnSnS$_4$( A at thickness 100 Å and B at thickness 1000 Å, Gmax 2.51/Å, voltage 100V) and ZnS(C at thickness 1000 Å, Gmax 4.5 1/Å; voltage 100V) are shown. And the four parts in the red rectangles correspond to the zoomed in parts in Figure 5.

These patterns are also called Zone Axis Pattern (ZAP) when they are aligned at certain zone axis, <0,0,1> in this situation. Each point in the central CBED disk corresponds to a different incident beam direction, and defines a family of conjugate points differing by reciprocal lattice vectors.

The features in ZAPs when the specimen is not thick enough are broad and diffuse features within the discs due to less diffraction and re-diffraction (A in figure 3). When the specimen is sufficiently thick, sharp lines within and outside the disc can be seen and these lines can be used for calculation of symmetry (B and C in figure 3). These lines are Laue Zone lines. A calculation of point group form CBED pattern is demonstrated here.

From Eades(1988), the four pieces of information contained in ZAPs that can be used to determined point group are bright-field symmetry (BF full), i.e. the symmetry of the sharp higher order Laue Zone (HOLZ) lines within the central disc; projection bright-field symmetry (BF proj), i.e. the symmetry of the broad features within the central disc; the symmetry of the whole pattern (WP full), i.e. the symmetry of the HOLZ lines and HOLZ Kikuchi lines in the pattern as a whole; the projection symmetry of the whole pattern (WP proj), i.e. the symmetry of the broad features in the zero-layer discs. Form these four pieces of information, diffraction group of the material can be decided of which a few point groups are corresponded.

The following figures helped to decide the symmetries.
Take ZnS as an example (refer to C of Figure 4 and C and D of Figure 5), both BF proj and WP proj of this ZnS sample can be read from the figures to be 4mm which lead to a 4mm1_R projection diffraction group (Eades’ 1988). The BF full of this ZnS is 4mm and WP full is 2mm thus the diffraction group is 4_Rmm_R. From Eades’ table, this diffraction group is corresponding to point groups 42m and 43m. However, ZnS is of cubic structure from its diffraction pattern previously, so the point group can only be 43m. Similarly, the point group of the Cu_2ZnSnS_4 can be calculated to be 4/mmm (using A and B of Figure 3 and Figure 4). The process of finding point groups of these two samples are summarized in Table 1 and Table 2.

Table I. Projection diffraction groups and the projection (2D) symmetries of CBED

<table>
<thead>
<tr>
<th>Projection diffraction group</th>
<th>Symmetry of 2D information</th>
</tr>
</thead>
<tbody>
<tr>
<td>WP proj</td>
<td>BF proj</td>
</tr>
<tr>
<td>4mm1_R (ZnS &amp; Cu_2ZnSnS_4)</td>
<td>4mm</td>
</tr>
</tbody>
</table>

Table II. Diffraction groups and the full (3D) symmetries of CBED patterns

<table>
<thead>
<tr>
<th>Diffraction group</th>
<th>Symmetry of high-order information</th>
<th>Projection diffraction group</th>
<th>Point group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WP full</td>
<td>BF full</td>
<td></td>
</tr>
<tr>
<td>4_Rmm_R (ZnS)</td>
<td>2mm</td>
<td>4mm1_R</td>
<td>42m &amp; 43m</td>
</tr>
<tr>
<td>4mm1_R (Cu_2ZnSnS_4)</td>
<td>4mm</td>
<td>4mm1_R</td>
<td>m3m &amp; 4/mmm</td>
</tr>
</tbody>
</table>

Assume a new crystal is discovered, we can get all the lattice parameters from XRD, thus a CBED pattern can be simulated and more information about this new crystal can reviled in a relatively short time.

CONCLUSION
Diffraction pattern simulation was studied. CBED patterns were simulated and analysis based on these patterns reviled the point group and other information of these crystals.

REFERENCES