Available online at www.sciencedirect.com
SCIENCE @ DIRECT®
ultramicroscopy
Ultramicroscopy 98 (2004) 187–193
www.elsevier.com/locate/ultramic

TRICE – A program for reconstructing 3D reciprocal space and determining unit-cell parameters

Xiaodong Zou[a,]*, Anders Hovmöller[b], Sven Hovmöller[a]

[a] Structural Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden
[b] College of Engineering Kista, Royal Institute of Technology, SE-164 40 Kista, Sweden

Received 7 January 2003; received in revised form 28 March 2003

Dedicated to Professor Fang-hua Li on the occasion of her 70th birthday

Abstract

A program system—Trice—for reconstructing the 3D reciprocal lattice from an electron diffraction tilt series is described. The unit-cell parameters can be determined from electron diffraction patterns directly by Trice. The unit cell can be checked and the lattice type and crystal system can be determined from the 3D reciprocal lattice. Trice can be applied to all crystal systems and lattice types.

PACS: 07.05.Pj; 07.78.+s; 42.25.Fx; 42.40

Keywords: Electron diffraction; 3D reconstruction; Unit-cell determination; Image processing

1. Introduction

Determination of crystal unit cell is the first and an important step of ab initio structure determination. For micro- and nano-crystalline powder samples, this is often very difficult by X-ray diffraction, especially when the sample contains several different phases. In contrast, it is easy to obtain single-crystal electron diffraction patterns of individual micro/nano-sized crystals in transmission electron microscopes. Due to the very short electron wavelength (~ 0.02 Å), an electron diffraction pattern is an undistorted representation of a 2D section of the 3D reciprocal lattice. The 3D reciprocal lattice can be obtained by tilting the crystal in the microscope and collecting a series of diffraction patterns from the same crystal.

In practice, it is not easy to reconstruct the 3D reciprocal lattice and determine the unit-cell dimensions manually from the diffraction pattern series. We have developed a program system—Trice—for this purpose. Electron diffraction patterns are digitised into a PC. The position and intensity of each diffraction spot from each diffraction pattern in the tilt series are determined and refined by the program system ELD [1–2]. These data plus the direction of the tilt axis and angle of tilt are used as input for Trice.

---

*Corresponding author. Tel.: +46-8-16-23-80; fax: +46-8-16-31-18.

E-mail address: zou@struc.su.se (X.D. Zou).

0304-3991/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.ultramic.2003.08.025

2. Method and results

2.1. Recording and digitising ED patterns

Three or more ED patterns are taken from the same crystal. Usually the crystal is tilted along one common (short) reciprocal axis. The tilt angles (*x,y*) from the goniometer are written down. It is convenient, but not necessary if all ED patterns are recorded using the same camera length. The tilt series does not need to have the same common axis. However, it has to be tilted from the same zone axis, i.e. all the common axes should be present in one ED pattern in the series. A typical example of a tilt series of ED patterns is shown in Figs. 1a–d. The sample is $Li_2NaTa_7O_{19}$ [3].

When a double-tilt specimen holder is used, the angle θ between two ED patterns taken from the same crystal, with the angles (x_1, y_1) and (x_2, y_2), respectively, is

$$\theta = \cos^{-1}(\cos x_1 \cos y_1 \cos x_2 \cos y_2 + \cos x_1 \sin y_1 \cos x_2 \sin y_2 + \sin x_1 \sin x_2). \quad (1)$$

When a rotation-tilt specimen holder is used, the angle θ between two ED patterns taken from the same crystal, with the tilt (x) and rotation (y) angles (x_1, y_1) and (x_2, y_2), respectively, is

$$\theta = \cos^{-1}(\sin x_1 \cos y_1 \sin x_2 \cos y_2 + \sin x_1 \sin y_1 \sin x_2 \sin y_2 + \cos x_1 \cos x_2). \quad (2)$$

The ED patterns are digitised either using an on-line CCD camera or off-line. Before processing the ED pattern, information about the conditions under which the ED pattern was taken and digitised should be given in order to determine the cell parameters. These are: the accelerating

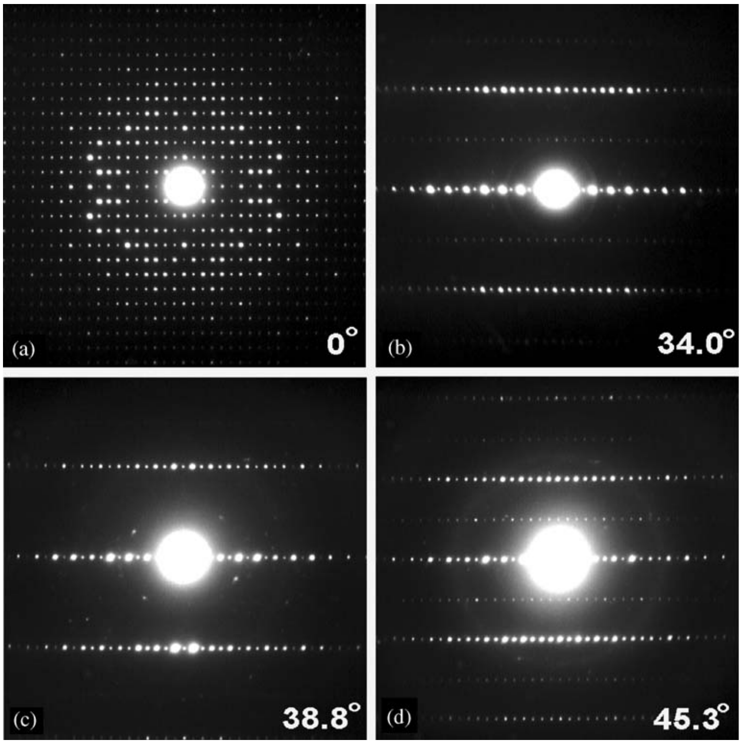


Fig. 1. Electron diffraction patterns of $Li_2NaTa_7O_{19}$ from a tilt series of the same crystal. The common tilt axis is horizontal. The tilt angles related to (a) are 34.0° for (b) 38.8° for (c) and 45.3° for (d).

voltage, camera length (L, normally needs to be calibrated), digitisation constant (M, the number of pixels that corresponds to 1 mm on the CCD camera or negative film) and possibly the aspect ratio X/Y (ratio of the magnifications along the horizontal and vertical directions).

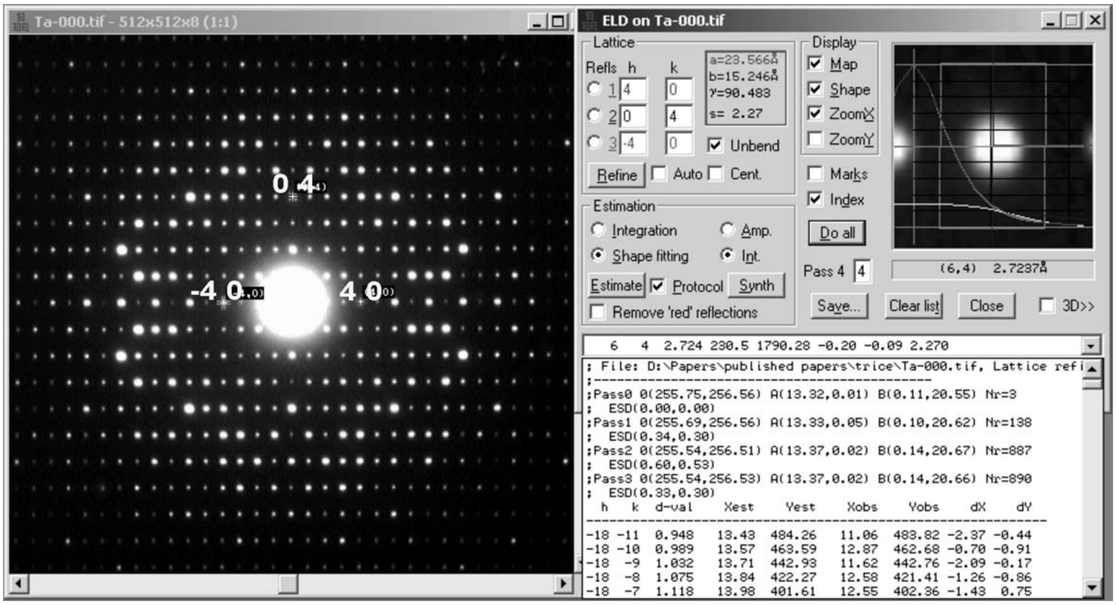
The digitisation constant (L, pixels/mm) and the aspect ratio X/Y can be calculated from an ED pattern with known d-values, preferably powder rings. It has to be digitised with the same conditions as the tilt series. If photographic films are digitised off-line, the digitisation constant and the aspect ratio X/Y can be calculated from a millimetre graph paper, digitised under the same condition as the photographic films.

2.2. 2D ED processing by ELD

Before reconstructing the 3D reciprocal space, the positions and intensities of all the diffraction spots on each ED pattern are determined. This is done using the program ELD [1–2].

Firstly, one has to select three reflections and give their indices in 2D. The positions of the central spot (000 reflection) and the two basic reciprocal vectors of the ED pattern are calculated from the three indexed reflections and then refined by a least-squares procedure using all the reflections on the ED pattern (Fig. 2). If the digitisation constant M, the camera length L and the electron wavelength λ are known, the ED constant ($= ML\lambda$, Å∗pixel) is calculated from these data. The 2D lattice parameters (a, b and γ) are then calculated from the reciprocal lattice vectors and the ED constant. The slight distortions of the reciprocal lattice caused by the curvature of the Ewald sphere and the digitisation are compensated for by an unbending function in ELD.

ELD estimates the intensity of each reflection, using a shape fitting procedure. The shape of the diffraction spots is first estimated using all those reflections that are not saturated and then further refined in four cycles. If nearly all the reflections in



```
a=23.566Å
b=15.246Å
γ=90.483
s= 2.27
```

```
   6   4  2.724 230.5 1790.28 -0.20 -0.09 2.270
; File: D:\Papers\published papers\trice\Ta-000.tif, Lattice refi
;------------------------------------------
;Pass0 0(255.75,256.56) A(13.32,0.01) B(0.11,20.55) Nr=3
;  ESD(0.00,0.00)
;Pass1 0(255.69,256.56) A(13.33,0.05) B(0.10,20.62) Nr=138
;  ESD(0.34,0.30)
;Pass2 0(255.54,256.51) A(13.37,0.02) B(0.14,20.67) Nr=887
;  ESD(0.60,0.53)
;Pass3 0(255.54,256.53) A(13.37,0.02) B(0.14,20.66) Nr=890
;  ESD(0.33,0.30)
  h   k  d-val    Xest    Yest    Xobs    Yobs    dX    dY
-----------------------------------------------------------------
-18 -11  0.948   13.43  484.26   11.06  483.82 -2.37 -0.44
-18 -10  0.989   13.57  463.59   12.87  462.68 -0.70 -0.91
-18  -9  1.032   13.71  442.93   11.62  442.76 -2.09 -0.17
-18  -8  1.075   13.84  422.27   12.58  421.41 -1.26 -0.86
-18  -7  1.118   13.98  401.61   12.55  402.36 -1.43  0.75
```

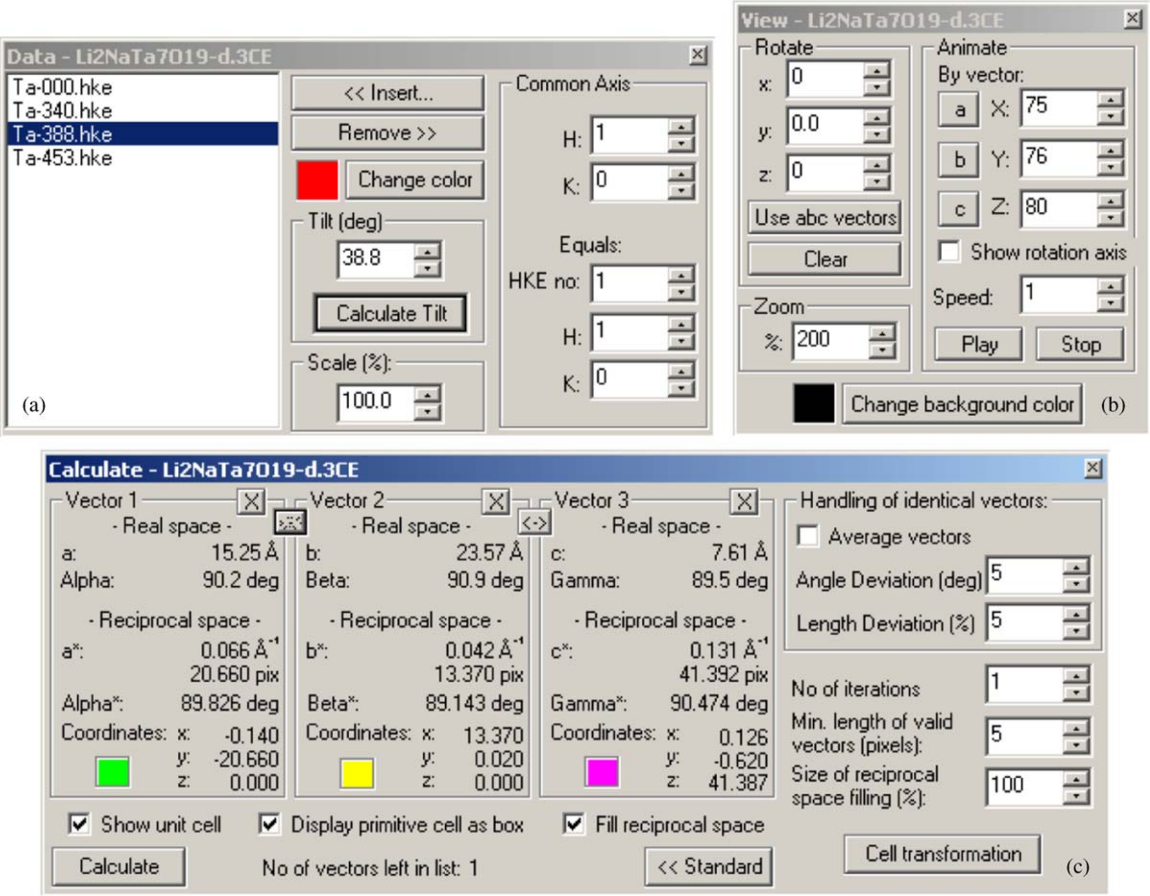
Fig. 2. Processing of an electron diffraction pattern by ELD. (a) Three reflections (here (4 0), (0 4) and (−4 0)) are chosen and their indices are given by the user. The common axis is indexed as *(h 0)* for all ED patterns in the series. (b) The positions of the (0 0), (1 0) and (0 1) reflections are first calculated from the indices of the three reflections and then refined in three cycles using all reflections. If the ED pattern is calibrated (as it is here), the unit-cell dimensions in projection (a, b and γ) and the corresponding d-values of all reflections will be calculated. The intensity of each reflection is estimated using a shape fitting procedure, which compensates for saturation and the non-linearity of the CCD camera.

an ED pattern are saturated, the shape fitting procedure will not work. In such a case, the intensity is estimated simply by integration. The positions and intensities of all reflections can be saved in a file with extension .hke.

2.3. Reconstructing 3D reciprocal space

Trice combines several 2D electron diffraction patterns, with the positions and intensities given by ELD, into 3D reciprocal space. Trice runs under Windows95, 98, 2000, NT and XP. It is written in C++ and uses OpenGL [4] to visualise the electron diffraction spots in 3D reciprocal space. The positions and intensities of all reflections for each zone axis (saved as .hke files) are read into Trice (Fig. 3a). The first ED pattern is used as a reference and the other ones are automatically scaled to the first pattern using the common axis/axes. The tilt angle of an ED pattern related to the first one is calculated by Trice using the expressions (1) or (2) above.

The 3D reciprocal space can be visualised and animated in any directions (Fig. 4) using the View option (Fig. 3b). It is possible to zoom the 3D electron diffraction pattern and change colours of the background and the diffraction spots of each 2D pattern.



Data - Li2NaTa7O19-d.3CE

Ta-000.hke
Ta-340.hke
Ta-388.hke
Ta-453.hke

Tilt (deg): 38.8
Scale (%): 100.0
Common Axis H: 1 K: 0
Equals: HKE no: 1 H: 1 K: 0

View - Li2NaTa7O19-d.3CE

Rotate x: 0 y: 0.0 z: 0
Zoom %: 200
Animate By vector: a X: 75 b Y: 76 c Z: 80
☐ Show rotation axis
Speed: 1

Calculate - Li2NaTa7O19-d.3CE

	Vector 1	Vector 2	Vector 3
- Real space -	a: 15.25 Å	b: 23.57 Å	c: 7.61 Å
	Alpha: 90.2 deg	Beta: 90.9 deg	Gamma: 89.5 deg
- Reciprocal space -	a*: 0.066 Å^{-1}	b*: 0.042 Å^{-1}	c*: 0.131 Å^{-1}
	20.660 pix	13.370 pix	41.392 pix
	Alpha*: 89.826 deg	Beta*: 89.143 deg	Gamma*: 90.474 deg
Coordinates: x:	-0.140	13.370	0.126
y:	-20.660	0.020	-0.620
z:	0.000	0.000	41.387
	🟩	🟨	🟪

Handling of identical vectors:
☐ Average vectors
Angle Deviation (deg) 5
Length Deviation (%) 5
No of iterations 1
Min. length of valid vectors (pixels): 5
Size of reciprocal space filling (%): 100
☑ Show unit cell
☑ Display primitive cell as box
☑ Fill reciprocal space
No of vectors left in list: 1

Fig. 3. (a) The positions and intensities of each electron diffraction pattern are used as input to Trice and the tilt series is combined into one 3D lattice according to the common axis and tilt angles. Here the four ED patterns in Fig. 1 are combined. (b) The 3D lattice can be rotated along either the x, y and z axes or the basic vectors $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$, determined by Trice. (c) The unit-cell parameters a, b, c, alfa(α), beta(β) and gamma(γ) are calculated from the three shortest reciprocal vectors.

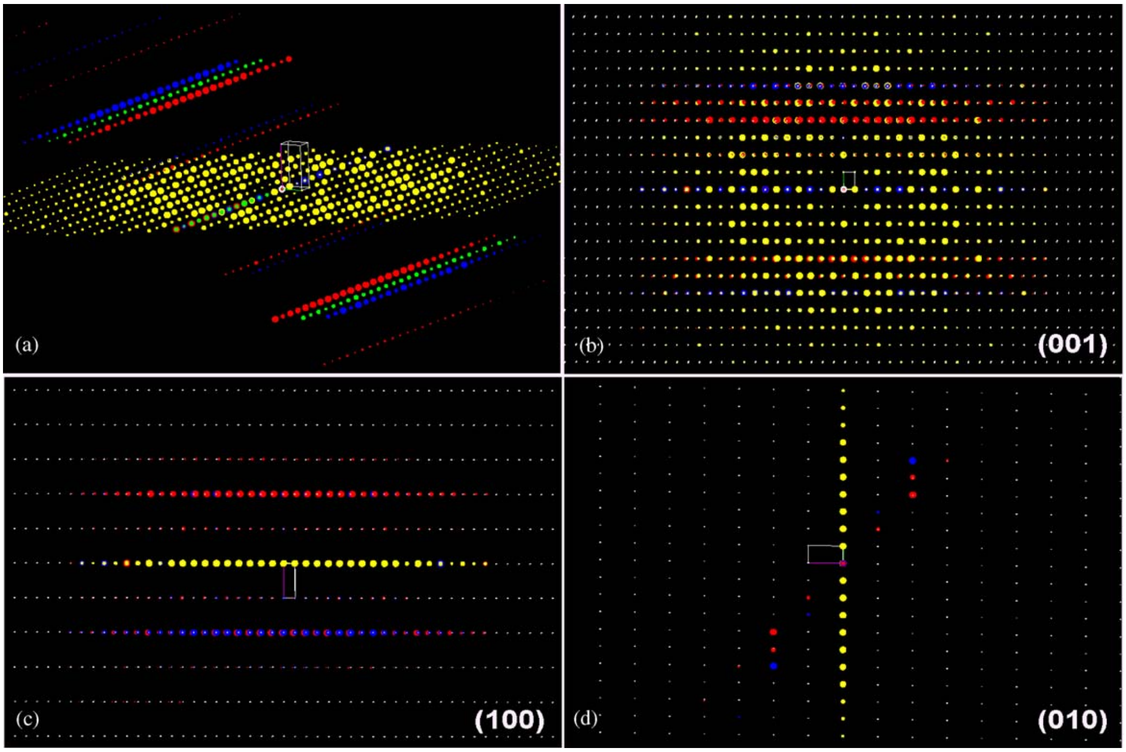


Fig. 4. 3D reciprocal lattice reconstructed by Trice from the four electron diffraction patterns (a)–(d) in Fig. 1 viewed along (a) an arbitrary direction, (b) the ***c****-axis, (c) the ***a****-axis and (d) the ***b****-axis. Since the projections of the 3D reciprocal lattice are primitive along all three basic axes (b)–(d), the whole 3D lattice is also primitive.

2.4. Determining the unit cell

The algorithm for finding the unit cell is rather straightforward, i.e. to find the three shortest 3D vectors which are linearly independent. It starts off with the two basic 2D vectors ***a**** and ***b**** from each inserted ED pattern. These vectors are converted into 3D vectors according to the tilt angles and included in a list. Those vectors whose angles differ from each other by less than a user-defined angle (for example 5°) and whose lengths differ from each other by less than a user-defined percent (for example 5%) are considered to be identical and only one of them (or their average) is kept. Then all linear combinations of those vectors on the list are generated and those that are shorter than the original vectors are added to the list. The expanded list is then checked again by Trice to remove all identical vectors.

Finally, the three shortest vectors are chosen from the list and the volume of the reciprocal unit cell generated by those three vectors is calculated. If the volume is less than 20% of the product of the lengths of the three vectors, the third shortest vector is replaced by the next shortest vector and the volume is checked again. This continues until the volume is large than 50% of the product of the lengths of the three vectors. The three selected vectors are now considered to be the basic vectors of the unit-cell. The unit-cell dimensions (a, b, c, α, β and γ) are calculated from these three reciprocal vectors and can be displayed (Fig. 3c).

Since Trice tries to find the three shortest vectors in the reciprocal lattice, it works equally well for all crystal systems and lattice types [5]. The correctness of the unit cell determined can be easily judged in Trice. The 3D ED pattern is oriented to be parallel to each of the three reciprocal axes using the View option, as shown in Figs. 4c and d. If the unit cell is correct, all diffraction spots should appear at the lattice points.

Since all ED patterns in a series are scaled to the first ED pattern of the series, the accuracy of the unit-cell dimensions obtained by Trice depends on how well the camera length and the digitisation constant are calibrated for the first ED pattern. From our experience, the error can be up to 5% for an uncalibrated ED pattern and this may be reduced to less than 2% if the ED pattern is calibrated using a known compound or from powder rings of for example gold or aluminium. However, large errors can result from inaccurate tilt angles, which can exceed to a few degrees and are more difficult to calibrate. Thus, it is very important to minimise the errors from the tilt angles, for example by always tilting the crystals in the same tilt directions, and after each tilt series, rechecking the tilt angles (x,y) of the first ED pattern from the goniometer to see if there are any angle shifts.

The possible errors of the tilt angle can be easily detected from the 3D electron diffraction pattern reconstructed by Trice. When the 3D electron diffraction pattern is aligned along a zone axis, all diffraction spots at different tilt angles should appear exactly on top of each other, as shown e.g. in Figs. 4b and c. If the tilt angle of an ED pattern had been wrong, the diffraction spots from this pattern would deviate from the lattice position of the 3D reciprocal space. If one first orients the common tilt axis to be parallel to the view window and then rotates the 3D electron diffraction pattern along the common axis to a zone axis, the deviation of the diffraction spots on this ED pattern from the others would be easily detected, and the tilt angle could be adjusted visually.

In the case of $Li_2NaTa_7O_{19}$ shown here, the unit-cell dimensions obtained were $a = 15.25$, $b = 23.57$, $c = 7.61$ Å, $\alpha = 90.2°$, $\beta = 90.9°$ and $\gamma = 89.5°$, compared to those obtained by X-ray powder diffraction $a = 15.231(1)$, $b = 23.573(1)$, $c = 3.837(0)$ Å and $\alpha = \beta = \gamma = 90.0°$ [3]. The periodicity in the c-axis determined by ED diffraction is twice as long as that determined from X-ray powder diffraction. This doubling can be explained as a modulation (superstructure) along the c-axis, possibly due to the ordering of the cations Li^+ and Na^+. This modulation only gives rise to very week reflections hkl with $l = 2n+1$ that were not detected by X-ray powder diffraction (see Fig. 1b and d).

As mentioned above, the unit-cell parameters obtained by Trice is not very accurate and need to be refined. The refinement should be done independent of the tilt angles, which cause the largest errors in unit-cell parameters. Once the unit cell is determined, it is possible to index all ED patterns within and outside the tilt series and obtain the correct 3D indices of the two basic reflections on each ED pattern. This can be done automatically using the program for phase identification PhIDO [6]. The unit-cell parameters can then be refined from those reflections generated from the basic reflections from each ED pattern and the corresponding d-values obtained by ELD [2]. This option is, however, not yet implemented in the present version of Trice.

2.5. Determining the lattice type by Trice

Trice finds only the reduced unit cell (formed by the three shortest vectors). If the lattice is not primitive but centred, one has to deduce the correct unit cell according to the symmetry of the 3D electron diffraction pattern. This can be done by first checking the 3D reciprocal space to determine the lattice type.

The lattice type that a crystal belongs to can be determined from the systematic absences of the 3D reciprocal lattice. Figs. 4b–d show the 3D reciprocal lattice projected along the three main axes and no systematic absences for the general reflections (hkl) are observed. This indicates that the lattice of $Li_2NaTa_7O_{19}$ is primitive.

In the case that α, β and γ are not close to 90°, the possible lattice centring may be found by viewing the reciprocal lattice, as shown in Fig. 5. A primitive unit-cell can be transformed to a centred unit-cell by Trice. The centred unit cell parameters $\boldsymbol{b}_c^*$ and $\boldsymbol{c}_c^*$ are recalculated from the centred reciprocal lattice, e.g., $\boldsymbol{b}_c^* = (\boldsymbol{b}_p^* - \boldsymbol{c}_p^*)/2$ and $\boldsymbol{c}_c^* = (\boldsymbol{b}_p^* + \boldsymbol{c}_p^*)/2$ (see Fig. 5).

3. Conclusion

Trice combines electron diffraction patterns of different orientations and reconstructs a part of

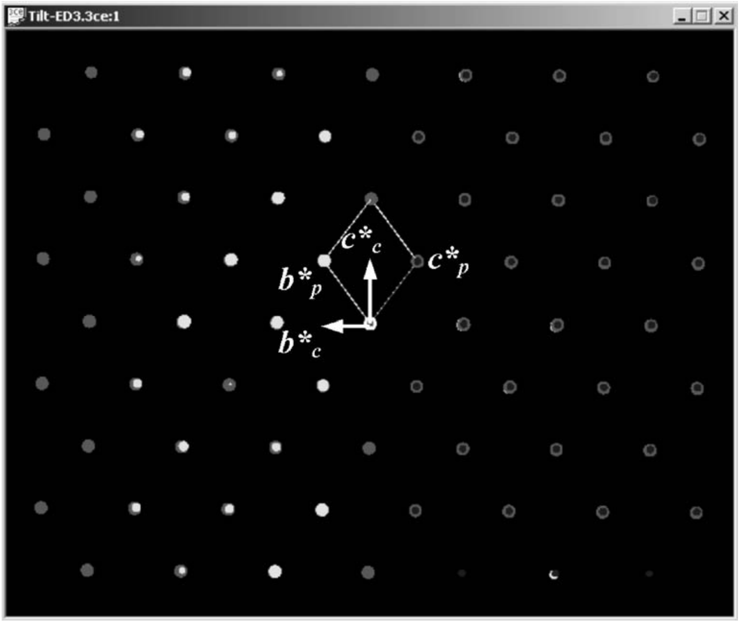


Fig. 5. Example of a centred 3D reciprocal lattice reconstructed by Trice from three electron diffraction patterns. Once the transformation matrix between the new and old reciprocal vectors are given, the unit-cell parameters of the new centred unit cell will be calculated by Trice.

the 3D reciprocal lattice. The 3D reciprocal lattice can be rotated and visualised from any direction. The unit-cell parameters can be determined from electron diffraction patterns directly by Trice. In most cases, diffraction patterns from three different orientations are sufficient for determining the unit cell. The lattice type and crystal system can be determined from the 3D reciprocal lattice. The unit-cell parameters can be further refined against the *d*-values of reflections from a number of calibrated ED patterns or X-ray powder diffraction data to higher accuracy. Trice can be applied to all crystal systems and lattice types.

Acknowledgements

This study was supported by Grants from the European Commission to the project New Frontiers in Structural Biology and from the Swedish Research Council (VR). Xiaodong Zou is a Research Fellow of the Royal Swedish Academy of Sciences supported by Alice and Knut Wallenberg Foundation.

References

[1] X.D. Zou, Y. Sukharev, S. Hovmöller, Ultramicroscopy 49 (1993) 147.
[2] X.D. Zou, Y. Sukharev, S. Hovmöller, Ultramicroscopy 52 (1993) 436.
[3] G. Grins, L. Banos, D.C. Sinclair, A.R. West, J. Mater. Chem. 4 (1994) 445.
[4] http://www.opengl.org.
[5] M. Vippola, J. Keränen, X.D. Zou, S. Hovmöller, T. Lepistö, T. Mäntylä, J. Am. Ceram. Soc. 83 (2000) 1834.
[6] PhIDO—Phase identification and indexing from ED patterns, Calidris, Sollentuna, Sweden, 2001, www.calidris-em.com.