

# Consistent indexing of a (set of) single crystal SAED pattern(s) with the ProcessDiffraction program

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## Abstract

A computer program called “ProcessDiffraction” helps indexing a set of single crystal selected area electron diffraction (SAED) patterns by determining which of the presumed structures can fit all the measured patterns simultaneously. Distances and angles are measured in the digitalized patterns with a graphical tool by clicking on the two shortest non-collinear vectors (spots), using user-supplied calibration data. Centers of the spots and center of the pattern are optionally refined by the program. Suggested individual indexing solutions (consistent with an assumed unit cell) are listed by the program for each pattern. Simulated patterns are also consulted to check if the shortest calculated distances coincide with measured ones. Common solutions for the set are selected by checking the angles between the suggested zone axes against the angles between the experimental goniometer settings. The indexing process is manually controlled by selecting the candidate structures (one-by-one) for indexing and by specifying the tolerances for  $d$ -values, plane angles and zone angles. Patterns of any crystal system can be indexed successfully. Although error bars are larger in electron diffraction than in X-ray diffraction (XRD), frequently, many unrelated indexings are possible for any one electron diffraction pattern (irrespective of the indexing method), a set of SAED patterns can generally be indexed unambiguously, i.e. the three-dimensional reciprocal space can be identified correctly. Two other tools also help planning tilting experiments: zones along a plane can be listed (with their angles extended from a pre-selected zone in that plane) and zones lying at a given angle (specified with a tolerance) from a zone can also be identified (as they are situated between two cones). Another tool searches the XRD database directly either for advice on possible structures for a composition or to help calibration.

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## 1. Introduction

Electron microscopists frequently encounter the need to identify individual microscopic-sized crystallites, i.e. to identify the crystallographic phase the crystallite corresponds to. Structure determination is generally based on selected area electron diffraction (SAED) patterns in the transmission electron microscope (TEM). Due to the presence of electromagnetic lenses in the TEM, the accuracy of the measured  $d$ -values and the angles between the reflections is inferior to the accuracy common in X-ray diffraction (XRD). As a consequence, phase identification, based on a single SAED pattern is not reliable enough, since several three-dimensional (3D) reciprocal lattices may have at least one two-dimensional (2D) slice that coincides with the measured one within the error bars common in SAED. The more slices in different directions are taken (by recording a tilt series of diffraction patterns), the less probable that more than one 3D lattice has all the specified slices within the experimental errors. It is especially true if tilting is carried out along two perpendicular axes (in contrast to tilting around only one axis). So, the preferred way of phase identification of single crystal grains is to index all the patterns from one (or more) tilting series as a unified set. One tilting series preferably goes along a Kikuchi band, so a row of reflections is common within that series. Indexing of the entire set can progress in two alternative ways. The above remarks apply to both of them.

One way is to try to merge the measured data into a 3D set and determine the unknown cell type and cell parameters from the measured sub-set of the unknown 3D reciprocal lattice [1,2].

The other way (elaborated in this paper) is based on the fact that in most of the cases a short-list of candidate phases is known in advance and phase identification only confirms which one of them corresponds to the measured grain (or proves which one of them does not fit). The program *ProcessDiffraction* [3–7] helps phase identification of single crystals by checking if the set of SAED patterns recorded with known goniometer settings can be indexed consistently with the reflections of a pre-selected Bravais lattice (with given cell

parameters). Suggestions for possible structures can be obtained from within *ProcessDiffraction* by consulting the Pdf-2 XRD database [10] using information about the elements present (from electron excited X-ray emission spectroscopy (EDS) or electron energy loss spectrometry (EELS)). The previous versions of the program [8] were only used for ring patterns, however, from version 3.5.0 upward the indexing of single crystal spot patterns (elaborated in this paper) is also incorporated. The new version will also be available free at the same website from autumn 2004.

Since diffraction methods are the most important sources of structure information, many previous approaches were published for obtaining structure-related parameters from electron diffraction patterns. Beside similarities, each of them is focused on one or more specific task(s) and offer advantages over the others. The short comparison below outlines the place of the new program among the existing related methods.

Hart [9] presents a search/match database approach to identify the phase, from which an electron diffraction pattern was recorded. He assumes that the three shortest diffraction vectors were successfully identified and measured, and the lengths of these vectors serve as a manual input to his program. He also assumes that the phase to be found is present at the NIST Crystal Data database. He does not examine either angular relationships or how the crystal was tilted to measure the three shortest vectors. The three numbers are measured off-line, separate from his program. Calibration of the patterns is also done independently of his program. In contrast to this, both the measurement and the calibration processes are integral parts of the present approach. Further differences are that both the angular relationships within any one pattern and the sample-tilt relations between several individual patterns are also used in the present approach. In order to find candidate structures, the present method offers suggestions by using a source different from the one used in Hart's approach: the Pdf-2 XRD database [10]. Phases with known qualitative elemental composition can be searched within the present method. The database is not

given together with the program, but its legal users can directly access the database from within ProcessDiffraction.

Narayan [11] presented a method and a computer program which is used in off-line evaluation of a single electron diffraction pattern. The off-line measured and calibrated lengths of three reciprocal vectors (which form a parallelogram) and the angles between them are the input values. All possible distances and angles, calculated for a pre-selected crystal structure, are listed by the program and compared to the measured ones using pre-defined tolerances. The possibility that two or more different crystal structures can yield solutions to the measured pattern (within the tolerance) is not examined in that paper. Individual patterns are also solved with this approach in the present method. One of the main new points in our approach is the simultaneous examination of a set of patterns, taking into account the tilting angle between their recordings. This later extension makes the solution unique in case of some patterns, when any one member of the set could be indexed with multiple structures, if the patterns were treated separately. The on-line measurement and calibration, together with the additional tools to plan the tilting experiment and to find the candidate structures make the new approach complete.

Wolczyr [12] presented a computer program for the reconstruction of the reciprocal lattice from a set of electron diffractograms. His approach takes the positions and intensities extracted from the individual diffraction patterns by the commercial CRISP program [13] and tries merging them into a single 3D set. 2D indexes are manually provided by the user. Visual tools are provided for rotation of the merged 3D-set and for fine-tuning of the nominal goniometer settings (where the patterns were recorded), in order to make the supposedly identical points to coincide. The unit cell is determined manually, by visual inspection of the merged set. The same algorithm is taken over in Zou's paper [2] to merge a series of 2D patterns into a 3D lattice and for tilt-angle correction. Zou went one step further than Wolczyr and determined the three shortest reciprocal lattice vectors by an automated procedure. In contrast to his

approach, the present method does not try building up the unknown reciprocal lattice unit cell, but tests if different presumed model structures can fit the set of measurements within the tolerances. Consequently, the errors, which originate from the limited accuracy of tilting, are not accumulated in the present method (especially far from the center), but assessed separately and individually as deviations between the measured and modeled angles between any pairs of zone axes. Another difference (originating from the different objectives) is that no manual indexing of the 2D patterns is needed in the present approach.

An even more general algorithm for determining the lattice type and lattice parameters has been presented by Belletti and coworkers [1]. In contrast to Zou's approach [2], the 2D indexing of the individual patterns is performed automatically. Additionally, there is no need for recording the series of patterns from the same crystallites with known goniometer settings. The program identifies the same vector in two patterns and assumes that the others differ only due to the tilting of the same structure and determine that tilt by a trial-and-error method. Their target again, the determination of the unknown unit cell parameters. As mentioned in the previous paragraph, our target and approach is different from that. (They also have a robust and delicate method for extracting accurate intensity values, but the latter is outside the scope of the present paper.)

Dimmeler and Schröder [14] present a sophisticated method to determine the orientation of large unit-cell organic crystals and biological material with very high accuracy. They measure not only the positions, but also the intensities of a very large number of diffraction spots and evaluate them individually by least-squares fitting. The high accuracy in tilting angles is needed, since a small error in angles causes an incorrect indexing of some spots in the very dense reciprocal space they examine, reducing the achievable resolution, when the measured structure factors are used in a synthesis. The high accuracy is achieved for a special geometry of flat-lying crystals with an iterative combination of measurement and simulation. Our simpler approach has less ambitious targets. In contrast to their elaborated electron

crystallography of organic materials, the present approach only identifies if an assumed unit cell is compatible with a set of measurements (and if it is the only compatible one from a finite set of possible candidate structures).

The software package of Zaefferer [15] contains several computer-aided tools for crystallographic analysis in the TEM. One of his tools, the determination of crystal orientation, is related to our present topic. Solutions are offered in his package by using either Kikuchi lines or spot patterns. For spot patterns, he assumes kinematic diffraction conditions. The measured intensities are also used to fine-tune the orientation, on the basis of normalized diffraction strength, which is assumed to show the deviation of the reciprocal lattice point from the Ewald sphere. His target is again different from ours. He examines defects in a strongly deformed, known system and wants to characterize these defects. For that purpose, he tries to determine the orientation of known crystals accurately. In contrast to this, the present approach wants to prove which of the possible crystal structures can yield all the measured patterns unambiguously.

## 2. The program

The ProcessDiffraction program is multifunctional software that runs under the MS-Windows<sup>®</sup> operating system. The program offers different tools to extract information from all kinds of SAED patterns. Only the functions relevant to our present topic are discussed in this paper. Operation of the program is shown on a worked example here. The used procedures are arranged in five groups: the graphical tool and procedures used to determine the center of the pattern and the diffraction vectors including calibration of distortions, the procedure to suggest structures if the elemental composition is qualitatively known, the algorithm to test the match between any one pattern and the examined structure, the constraints used to examine the individual patterns as members of a unique set and finally, some additional useful tools. The sections below elaborate these five groups of procedures one-by-one.

### 2.1. Measurement of the diffraction vectors and calibration

Digitized diffraction patterns from standard image format files (see Appendix A) are processed by the program. Measurement and calibration progress in the steps below.

Raw calibration data are entered *manually*. These are accelerating voltage of the microscope, nominal camera length (mm), pixel size ( $\mu\text{m}$ ) or resolution of the scanner (pixels per inch), depending on the fact if a CCD or an Imaging Plate (IP) was used in the first case or if the pattern was digitized with a scanner in the second case. Digitized negatives are also processed by inverting the data first.

Fine-tuned calibration of the *camera length* can be done simply. Although this procedure is mainly used with powder pattern, it can also occasionally be used with single crystal patterns. When a known phase is measured, a simple clicking with the Mouse both on a selected diffraction line and on a Marker line (which is graphical representation of the calculated diffraction data) results in fine-tuned calibration of the roughly known camera length.

In order to measure the diffraction vectors, the *center of the pattern* is to be determined first. Center is determined iteratively. *Rough* centering is done by moving the pattern on the screen relative to a reference circle generated at a fixed position (at the center of the window). This kind of centering is primarily planned for ring patterns, but also works fine for spot patterns. Even in case of slight misorientation, when the spots are differently exposed (are of different size), it is straightforward to position the pattern so that the reference circle crosses the centers of symmetrically related spots. This way of positioning works well even if the center of the pattern cannot be seen (due to the application of a beam-stop to protect the CCD from overexposure). Both the magnification of the pattern (on the display) and the radius of the reference circle can be adjusted independently, facilitating convenient centering by any set of points. Default magnification and/or the position of the previously fixed center can be recalled easily (Fig. 1). The position of the center is

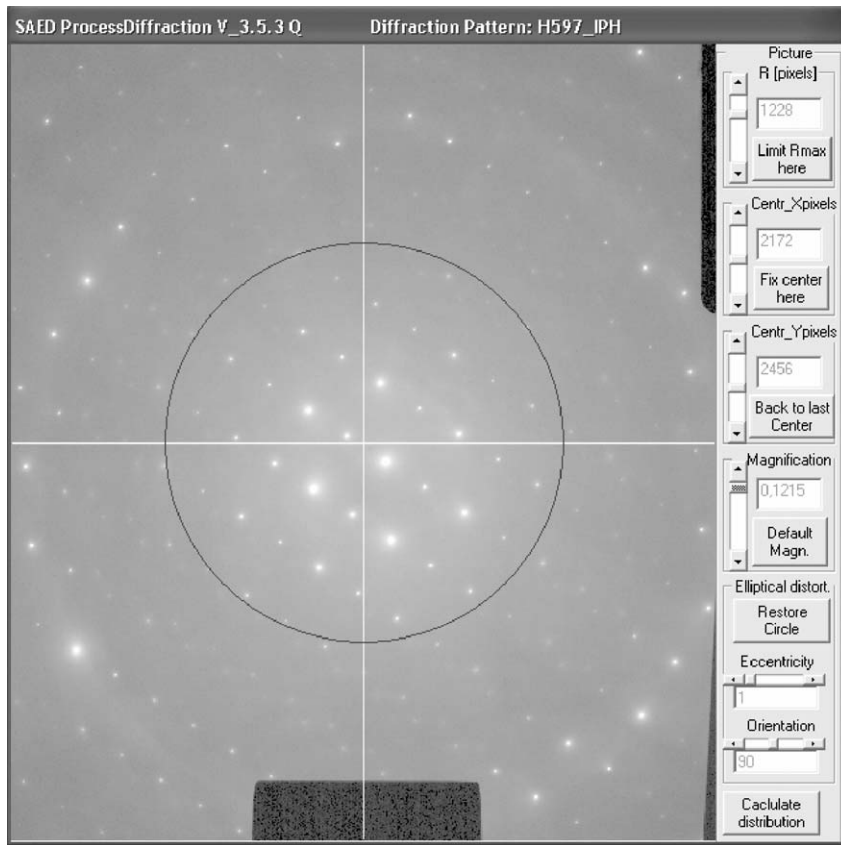


Fig. 1. Measured pattern (logarithmic intensity display) with reference circle and controls for centering and correcting for elliptical distortion.

fine-tuned iteratively later, during vectorization of the diffraction spots, after correcting for the elliptical distortion of the pattern first.

The most usual distortion that can be present in a pattern is an *elliptical distortion*, resulting in different scales at two, mutually perpendicular directions in the pattern. It originates from the imperfections of the lenses (and their alignment) and/or from the digitization process. The orientation of these axes can be in any direction, so incorporation of an “aspect ratio” (i.e. fixed vertical and horizontal directions) is not a satisfactory solution to the problem. Elliptical distortion can be corrected for in the ProcessDiffraction program by adjusting eccentricity and the direction of the axes independently (Fig. 1). The best way to perform the correction for the elliptical

distortion is to record a ring pattern under the same experimental conditions as the subsequent single crystal tilt series and adjust the parameters for elliptical correction in the ring pattern. The same parameters can be reused for the entire set of single crystal patterns recorded with the same microscope parameters (sample height, lens currents). Distances during later measurements are automatically corrected for this distortion using the calibrated parameters of the ellipsis (Fig. 1).

*Vectorization*, i.e. the measurement of the actual reflections is done by the software tool, called “*Cursor*”. The Cursor window is relocatable over the pattern to be measured (Fig. 2). Any of two points can be selected, but it is suggested that the two points with the shortest diffraction vectors be measured (the shortest first and the second

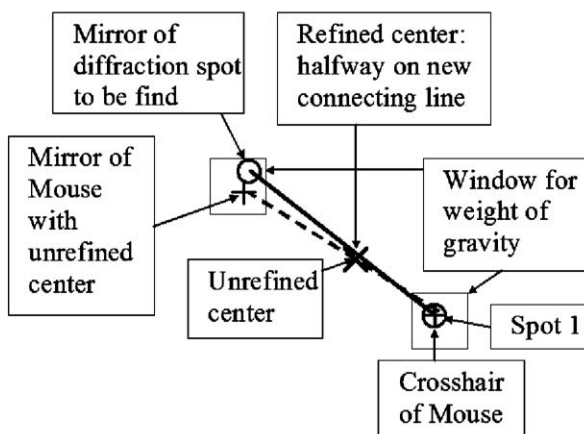
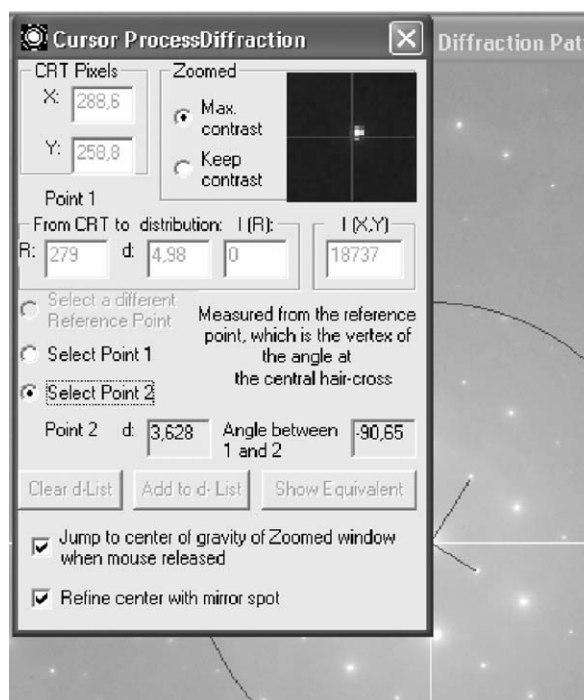


Fig. 2. (a) Cursor window shown over a part of the pattern. It is assumed that the center of the pattern has been roughly determined and fixed prior to activating this window. A magnified image of the area around actual Mouse position is shown in the upper right corner of the Cursor window. A pair of radio-buttons selects between two points (vectors) to measure. Two check-boxes determine if the actual Mouse-position help refine center position.  $d$ -values corresponding to the two measured reciprocal lattice vectors and the angle between them are also shown in the Cursor window. (b) Sketch of the principle how the mirror image is used to refine the center of the pattern.

shortest in counter-clockwise next). (Selection of the shortest vectors makes comparison to the simulated pattern easier later. In case of applying the beam-stop, selection of twice the shortest, etc. is suggested for the same reason, but not compulsory.) A magnified picture of the region around the actual Mouse position (within the pattern) is shown in a separate window in Cursor (Fig. 2). In the example in Fig. 2, point 1 corresponds to planes with a  $d$ -value of 4.98 Å, point 2 corresponds to 3.628 Å and the angle between the two vectors (pointing from the center of the pattern to the appropriate points) is 90.65°.

*Refinement* of the vectorized values is helped by two additional tools (two check-boxes). The selected point jumps into the *center of gravity* of the zoomed window (i.e. the selected spot) when the Mouse is released, if the first selection is checked. If the second one is also checked, the

center of the pattern is automatically *refined* by locating the spot at mirror position from the selected one, finding its center of gravity and appointing the center of pattern to the midsection between the two centers of gravity (of the selected point and the region around its mirror image), as delineated in Fig. 2b. The refinement is automatically iterated for the two pairs of selected points. Sub-pixel precision is achieved in that way.

A way of finding a shortlist of possible structures (which is needed for our indexing procedure) is given in the next section.

## 2.2. Obtaining suggested structures from the XRD database

In the present context, indexing means to find indexes in a pre-selected structure that give



distances and angles within the pre-specified tolerances. Several structures can easily be tested to see if the measured data are compatible with several of them or if they are unique within the examined structures. Possible structures are generally selected in accordance with knowledge of the elemental qualitative composition (latter taken from either EELS or from EDS, frequently called microanalysis). Since the Pdf-2 XRD database [10] also contains a lot of unit cell and space group data together with information about the elements present in a phase, it is also a useful source of structure information (additionally to being a source of diffraction data). ProcessDiffraction directly interfaces itself into the database whenever its legal availability is detected in a computer and data can be searched from within ProcessDiffraction. (The database itself is not part of our program but can be purchased independently from ICDD [10].) Several search profiles are available and structure data (Bravais lattice, cell parameters) can be extracted easily from within ProcessDiffraction.

### 2.3. Finding possible indexing for any one of the individual patterns separately

Indexing of any given pattern is done by comparing the measured vector lengths and angles to those calculated for the examined structure. Although we only selected two vectors directly (with one angle between them), additional three data are automatically determined by the program. The vector sum of the two measured and its two angles from the selected ones are also

measured and used in the indexing. Altogether, it means six measured quantities.

1.  $d$ -value of the first selected point (4.927 Å in Fig. 3). The direction of this vector serves as a reference direction later.
2.  $d$ -value of the second selected point (3.628 Å in Fig. 3).
3. Angle between the above two selected vectors (90.57° in Fig. 3).
4.  $d$ -value of the vector sum of the two selected values (2.8244 Å in Fig. 3).
5. Angle between 1 and 4 (53.1° in Fig. 3).
6. Angle between 2 and 4 (37.4 degrees in the example, not shown).

Bravais-lattice type and cell parameters, together with tolerances for the lengths of the vectors and for the angles between them are supplied manually (or can be loaded from a file). All lattice spacings (up to a given index) are calculated for a given structure.

First, individual lists of  $d$ -values in the vicinity of the measured ones (within tolerance) are created separately. Next, these lists are reduced to those elements of the lists, which give angles between the corresponding pairs in agreement with the measured angles. Finally, the indexes of the remaining reflections are tested against the selected vector-sum condition, which should also hold at the coordinate level (with reciprocal vector ( $h_3 k_3 l_3$ ) being the vector sum of ( $h_1 k_1 l_1$ ) and ( $h_2 k_2 l_2$ ), the coordinates must satisfy  $h_3 = h_1 + h_2$ ,  $k_3 = k_1 + k_2$  and  $l_3 = l_1 + l_2$ ). The final list contains the solution triplets, which satisfy all the

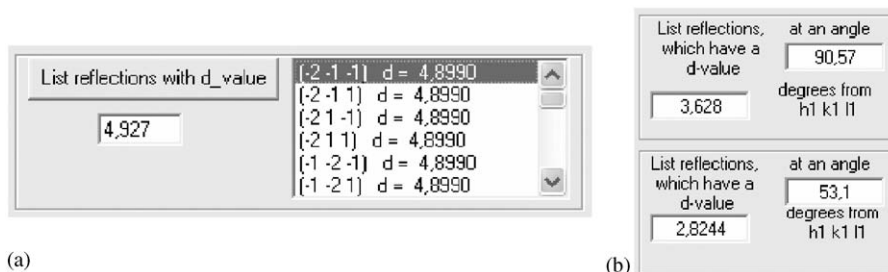


Fig. 3. The Crystallographic Calculator window with five of the above listed six measured values. As a first step, possible solutions for the first vector length are listed in (a).

Find Common Solution for which $h_4=h_1+h_3$ ; $k_4=k_1+k_3$ ; $l_4=l_1+l_3$			angle between $h_3\ k_3\ l_3$ and $h_4\ k_4\ l_4$	34,9
$(-2\ -1\ -1) + (-1\ -1\ 3) = (-3\ -2\ 2)$	Common Zone	$[-4\ 7\ 1]$		
$(-2\ -1\ -1) + (-1\ 3\ -1) = (-3\ 2\ -2)$	Common Zone	$[4\ -1\ -7]$		
$(-2\ -1\ -1) + (1\ 3\ 1) = (-1\ -4\ 0)$	Common Zone	$[-4\ 1\ 7]$		
$(-2\ -1\ -1) + (1\ 1\ -3) = (-1\ 0\ -4)$	Common Zone	$[4\ -7\ -1]$		

Fig. 4. The four symmetrically equivalent solutions for the indexing of the individual pattern, as suggested by the computer. The third in the list was selected in this example to serve as a constraint for later indexing the subsequent patterns.

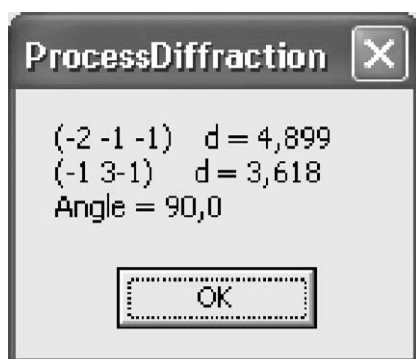


Fig. 5. Cross-checking of the selected solution. The two shortest reciprocal vectors in the simulated pattern are listed, also indicating the angle between them. It is in agreement with the measurement, where we also measured the two shortest vectors. In the example, the values are within specified tolerance, so the suggested solution is acceptable.

conditions above. For a given structure, these solutions are frequently symmetry-related equivalent solutions (like  $[\bar{4}\ 7\ 1]$  and  $[\bar{4}\ 1\ 7]$  in the example in Fig. 4).

For each of the possible solutions in the list, the zone axis, containing the given reflections is calculated.

As a means of cross-checking, the simulated pattern for that zone is examined and a message informs if the two shortest reciprocal lattice vectors in the given zone are really what we measured (Fig. 5). Manual control is also retained here, since the shortest vector may not be seen (cannot be selected experimentally) due to the application of the beam-stop. In that case the operator can easily judge if the measured one is a justified multiple of the calculated shortest.

Indexing with alternative structures can easily be tested by loading a new structure and requesting

recalculation from the program (without the need to re-measure anything).

#### 2.4. Applying common constraint for the entire set

Before applying the constraints, each member pattern of the set must be processed as explained above. Fig. 6 is an example list for the individual solutions for pattern 2.

As a next step, the measured angles between the goniometer positions (where the patterns were recorded) are calculated. A calculator for double-tilt holder is included in the program (Fig. 7).

Now, we can constrain which ones of the zone-axis solutions suggested for pattern 2 (in the unconstrained evaluation) is compatible with the experimentally measured angles between the zone axes. The computer can examine one-by-one for each pair of solutions, generated for the two individual patterns, if the constraint is satisfied. The list is reduced to those which are also compatible with this additional angle condition. Obviously, not all of the suggested solutions for one of the patterns can find a (zone-axis angle) matching pair in the second. (Picking one from the equivalent indexing possibilities from the first pattern fixes the coordinate system for the other. This condition determines which zone from the symmetrically equivalent ones (in the second pattern) is compatible with that fixing of the coordinate system.) For a given structure, the constraint for the zone axis generally allows only one solution (and its inverse, when all vectors are reversed) (Fig. 8).

Even if several crystal structures could yield indexing solutions for the individual patterns before the constraint, there is generally only one of them, which is also compatible with the



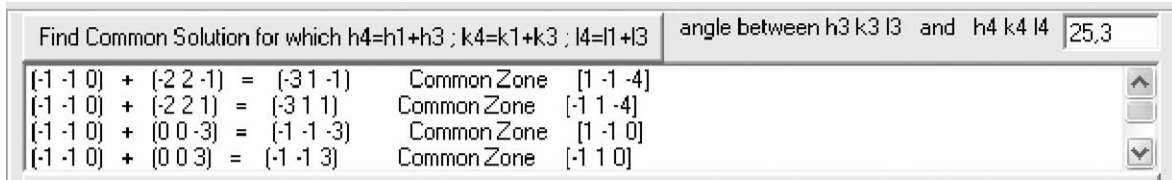


Fig. 6. Part of the list of possible solutions for pattern 2.

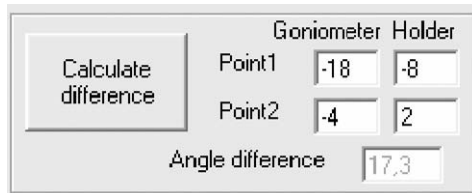


Fig. 7. Calculator to determine the angle between goniometer settings.

zone-axis condition. If more than one remained, further patterns from other zones (and the angles between the possible pairs of zones) must be taken into account. The larger the number of zones, the lesser the chance that another structure might exist that also has the same slices in the examined directions. Similar examination of more than two patterns is also suggested even if the first two seem to provide a unique solution. Introduction of the others serves as a means for cross-checking the data.

*Manual control* is important, because in case of no solution, the operator can immediately see which step is in error. Playing around with tolerances and checking the pattern, he/she can judge at once if the calibration of the camera length or of the elliptical distortion is wrong, or the accuracy in selection of the center is poor or, alternatively if the model (Bravais lattice) is not adequate for the given patterns.

## 2.5. Additional tools

The same tool, used above to reduce the list of possible solutions can also be used independently to locate other zones in a tilting experiment. Zones *at an angle* from any one selected zone can be listed (with a pre-selected angular tolerance). This tool

lists all the zones, which lie between the two cones determined by the tolerance (Fig. 9).

The second tool lists all the zones, which are found *along a plane* that was identified in the indexing of one of the individual patterns. The angles between the zones are again listed. It is automatically tested if the selected reference zone axis really lies in the specified plane. The plane common to the zones is easily selected together with the assumed solutions. The zones with a common plane must have a common  $d$ -value (appearing in the corresponding lists of both patterns) with a reciprocal lattice vector (reflection spot) pointing to the same direction in both patterns. One must remember that from the point of zones lying in a common plane, going along plane  $(h k l)$  and  $(n \times h n \times k n \times l)$  is the same thing (with  $n$  being a non-zero integer of either sign). The value of  $n$  only determines the length and sense of the plane normal, but does not affect the direction of the plane. The general condition for a zone to lie in a plane is that the plane normal must be normal to the zone vector too. Zones in the plane are selected by searching for zero scalar product of these two vectors (and this condition is not affected by a multiplier  $n$ ). This function helps planning tilting experiments by showing which zones can be expected when a pre-selected Kikuchi band is followed (subsequent to successful determination of the absolute orientation of the crystallite by prior indexing a few patterns) (Fig. 10).

The two conditions can also be applied simultaneously, providing list of zones, situated at the intersections of the plane with the area between the two limiting cones.

The Crystallographic Calculator window also contains a third tool that *converts* 3-index and 4-index indices into each other in hexagonal

Find Common Solution for which  $h_4=h_1+h_3$  ;  $k_4=k_1+k_3$  ;  $l_4=l_1+l_3$     angle between  $h_3 k_3 l_3$  and  $h_4 k_4 l_4$  25,3

$[-1 \ 1 \ 4]$

Reduce Result List to those, which satisfy the Zone condition below

Fig. 8. Only one solution for the second pattern remained after selecting one of the possible solutions for pattern 1 and applying the constraint for the angle between the zones.

Zone condition

☒ at an angle 15 from [ -4 7 1 ]

☐ also lie in the plane

List Zone axis, which are:

$[-5 \ 5 \ 1]$	15,2	Common plane (2 -1 15)
$[-4 \ 4 \ 1]$	15,4	Common plane (1 0 4)
$[-2 \ 5 \ 2]$	15,4	Common plane (3 2 -2)
$[-1 \ 3 \ 1]$	15,2	Common plane (4 3 -5)

Fig. 9. Zones found  $15 \pm 1^\circ$  from the pre-selected  $[\bar{4} \ 7 \ 1]$  zone in the examined cubic crystal structure. The actual angular distance values are also listed together with the zone indices.

Zone condition

☐ at an angle 15 from [ -1 1 4 ]

☒ also lie in the plane

List Zone axis, which are:

	h	k	l
$[-4 \ -3 \ -5]$	129,3	Common plane (1 -3 1)	
$[-2 \ -1 \ -1]$	106,8	Common plane (1 -3 1)	
$[-4 \ -1 \ 1]$	67,1	Common plane (1 -3 1)	
$[-3 \ -2 \ -3]$	123,6	Common plane (1 -3 1)	
$[-3 \ -1 \ 0]$	81,4	Common plane (1 -3 1)	
$[-1 \ -1 \ -2]$	140,3	Common plane (1 -3 1)	

Fig. 10. Example of part of a long listing of the planes that lie along plane  $(1 \ \bar{3} \ 1)$ . The angles indicated are measured from the  $[\bar{1} \ 1 \ 4]$  zone.

systems (Fig. 11). The appropriate controls are only activated when a hexagonal system is selected. Furthermore, it calculates  $d$ -values for planes with any Miller indices and angles between any two planes or any two directions, in any crystal systems.

## 2.6. Management of projects

The concept of “project” includes all the measured data loaded, all the evaluations performed and all the settings that control the appearances of the graphical presentations of data

Angle between directions

U1	V1	T1	W1		p1	q1	r1		p2	q2	r2		Angle
-1	1	0	4	<==>	-1	1	4	Calculate ==>					55,7
U2	V2	T2	W2										
1	4	-5	3		2	3	1						

☐ Specify directions with 4 indices
 ☒ Specify directions with 3 indices

Fig. 11. Example of converting 3-index and 4-index indices into each other, together with the calculation of angles between two arbitrary directions in the hexagonal system.

in the individual windows. In short, when the project is saved, the program execution can be interrupted and in a later moment continued from exactly the same conditions as if it had not been interrupted (by reloading the project).

The project concept also makes it possible to perform different processing of the same data and store each one under different project names (even though they might be based on the same measured pattern or set of patterns). For example, a measured and processed pattern can be compared to another set of data and to a (few) Markers and stored under one project name. In another project, the same processed pattern can be compared to another set of Markers and may contain a pattern indexed with the selected Markers, etc. This is more than if the picture of any window were saved at a given stage, because appearance can be quickly changed from within the project, while building up the project might mean much more work and time.

### 3. Advantages and limitations of the present approach

One of the advantages is convenient and quick testing of a complete set of measurements against several possible structures, to see if the entire set is consistent with all the measurements within the tolerances. After saving the project, the same set can later be tested against a new structure-hypothesis in a few seconds by reloading the project, loading a new structure into it, without the need to re-process the experimental data.

Selection of the four innermost points in a zone axis pattern (the two selected and their mirror images) introduces the *least distortion*. This is for two reasons. On the one hand, the central part (at small scattering angles) is less distorted than the outer parts. On the other hand, the simultaneous examination of both the selected spots and their mirror images made the procedure more *robust* and *reduced* the measured distortion considerably (as compared to when the center is determined separately, independently of the selected points, i.e. when no mirror images are used in the procedure). It can easily be tested that if the mirror-image procedure is used, it is generally enough to specify less tolerance (i.e. less distortion both in the vector-length and the angle) to find the correct solution than if the separate centering procedure is used (assuming the same pattern, the same operator and the same care).

By selecting the two shortest vectors, any spurious spots are automatically *neglected*. The same is true for reflections that might come from a different zone due to the presence of elongated reciprocal lattice points (“relrods”) and a dense reciprocal space. As a consequence, *errors* due to small deviations in tilting angle do not result in false points (in contrast to the method of merging sets into one 3D lattice), but instead, the error remains a separately handled error in the orientation of the sample during the exposure. These errors are easily identified when several zones are examined together and tested against tolerances.

There are *limitations* in the procedure, which determines the center of gravity of the selected spots. If there are several points that *overlap*

(e.g. due to the presence of an unwanted other grain that contributes to the pattern), the center of gravity mis-positions the spot. However, this procedure is optional and can be switched off, retaining the spot exactly at the position where it was selected manually.

Another limitation is if one tries to include a pattern, which is not a real zone axis pattern in the set. Obviously, a significant error must result in any attempt to interpret it as a zone axis pattern. However, careful setting during the experiment helps to avoid this type of error.

There are *general limitations*, which are not restricted to this method, but the experimenter must consider them (irrespective of the method he/she uses for the data evaluation). One of the general problems is that there exist structures which are very close to each other, so differentiation between them require special attention (even if it is possible). One example is a pair of hexagonal phases from the Ni–Ge system: Ni<sub>5</sub>Ge<sub>3</sub> (JCPDS 65-4812) has lattice parameters  $a = 3.913 \text{ \AA}$  and  $c = 5.064 \text{ \AA}$ , while Ni<sub>3</sub>Ge<sub>2</sub> (JCPDS 65-5541) has lattice parameters  $a = 3.948 \text{ \AA}$  and  $c = 5.036 \text{ \AA}$ . The author does not assume that such similar structures can be differentiated with electron diffraction, irrespective of the method used. The main reasons for that include not only calibration of the pattern (which can be fine-tuned) but also the presence of two types of distortions. One of the distortions is introduced by the *recording system* (microscope and digitization system) and (at least in principle) can be calibrated for. The other distortion is physical, i.e. originates from the sample, so the author cannot see a means to perfectly account for it. This second distortion comes from the fact that many of the thin films examined in a TEM are *strained* due to different reasons. That strain may not be homogeneous and isotropic. The ensuing changes in the positions and intensities of the diffraction lines are difficult to predict and can only be tried to be modeled if the system is known.

#### 4. Conclusions

A computer program is presented to help indexing a set of single crystal SAED patterns,

collected from the same crystallite in a TEM during one (or more) tilting series (around one or more tilting axes). A pre-selected phase (the model) is used in an attempt to index the set. Several models (phases) can be tested quickly and easily without the need to re-measure the data. Error tolerances can be specified independently for the length of the reciprocal vectors, for the angle between reciprocal vectors and for the angle between zone axes. The algorithm is semi-automatic, which facilitates retaining full operator-control during the entire process. The program can be applied to patterns corresponding to any crystal systems. Additional tools of the program also help manual computations and planning tilting experiments, as well as calibration and finding possible structures for a known composition.

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#### 5. Appendix A. : specificities of the current implementation of the program

##### A.1. Input data

Directories for the different input and output files can be specified by selecting “Options/File locations” from the menu. The User should start a session by specifying these directories.

The program accepts digitized patterns in Raw (\*.RAW), Bitmap (\*.BMP) or Tagged Image File (\*.TIF) format, or in any of the proprietary formats supported by either FUJI (\*.IMG) or

DITABIS (\*.IPL, \*.IPH, \*.IPC) imaging plate (IP) readers (the only two IP types available for TEM at the moment). Since CCD cameras can also produce TIF or BMP files and conventional film or print can also be digitized with a CCD camera, all types of usual data recording (film, CCD, IP) can be used directly with the program. Compressed image formats, leading to data loss are not supported. The original content of the file is used for data processing, while displayed content can be modified separately in order to enhance visibility. Visualization can be linear between limits, selected on the gray-level histogram, or can be equalized or can be logarithmic (for patterns with huge dynamic range). Calibration data, as accelerating voltage, camera length and pixel size (or scanner resolution in pixels/inch) are used to convert pixels into real-crystal-space or reciprocal space dimensions. Inverted data from a negative film can also be used directly. Both calibration data and lengthy additional information can either be supplied by the operator, or be read directly from the IP-files. These data are also stored together with the project and are automatically reloaded together with their corresponding pattern during later re-processing.

#### A.2. Usage of the XRD database

Since the database is not the part of the program, first a legal copy of the database must also be *installed* correctly on the same computer. During installation the user must follow the instructions given together with the database [10].

When the directory of the installed database is specified in the Options of ProcessDiffraction, a set on *index files must be generated* before the first usage. ProcessDiffraction uses its own index files, independent of those coming with the database. Generation of the indexes can be selected from the menu in the XRD panel within ProcessDiffraction. Although generation of the index files takes up to

30 min (depending on the computer), it is to be generated only once. The process *must not be interrupted*. If generation was interrupted by any reasons, it must be started from the beginning, since an incomplete set of index files results in incorrect listing of phases (e.g. other elements might remain in the listed phases, not only the selected ones; this is a sign that generation of index files was interrupted).

#### References

- [1] D. Belletti, G. Calestani, M. Gemmi, A. Migliori, Ultramicroscopy 81 (2000) 57.
- [2] X. Zou, A. Hovmöller, S. Hovmöller, Ultramicroscopy 98 (2004) 187.
- [3] J.L. Lábár, ProcessDiffraction: A computer program to process electron diffraction patterns from polycrystalline or amorphous samples, in: L. Frank, F. Ciampor (Eds.), Proceedings of EUREM 12, vol. III, Brno, 2000, pp. I379–I380.
- [4] J.L. Lábár, M. Adamik, Microsc. Microanal. 7 (Suppl. 2) (2001) 372.
- [5] J.L. Lábár, Microsc. Anal. (75) (2002) 9.
- [6] J.L. Lábár, M. Ishimaru, Y. Hirotsu, New possibilities in electron diffraction based phase analysis in the TEM, Proceedings of the Sixth Multinational Congress on Electron Microscopy, Pula, 2003, pp. 79–80.
- [7] J.L. Lábár, Role of electron powder diffraction in solving structures, Electron Crystallography, NATO ASI, Erice, 2004.
- [8] ProcessDiffraction can be downloaded free from <http://www.mfa.kfki.hu/~labar/ProcDif.htm>.
- [9] H.V. Hart, J. Appl. Crystallogr. 35 (2002) 552.
- [10] Pdf-2 X-ray diffraction database, International Center for Diffraction Data. <http://www.icdd.com>
- [11] C. Narayan, J. Electron Microsc. Tech. 3 (1986) 151.
- [12] M. Wolcyrz, M. Andruszkiewicz, WINREKS—a computer program for the reciprocal lattice reconstruction from a set of electron diffractograms, in: D.L. Dorset, et al. (Eds.), Electron Crystallography, Kluwer Academic Publishers, Dordrecht, 1997, pp. 427–430.
- [13] S. Hovmöller, Ultramicroscopy 41 (1992) 121.
- [14] E. Dimmeler, R.S. Schröder, J. Appl. Crystallogr. 22 (2000) 1088.
- [15] S. Zaefferer, J. Appl. Crystallogr. 33 (2000) 10.