On the Determination of Crystalline Orientation by Electron Diffraction

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The orientation of the crystal lattice relative to the specimen contours of a single crystal may be conveniently determined in an electron microscope using reflexion electron diffraction at grazing incidence. The practical procedure is described in some detail. As an example, the method was applied to a copper single crystal of unknown orientation. The results of 11 determinations with the crystal in as many different positions show that the experimental error of the method is of the order of 2° on individual measurements.

In research on crystalline solids it is frequently important to know how the crystal lattice is located relative to the specimen as defined by its contours. In some cases this may be inferred directly from the shape of the specimen whereas in other cases, especially with metals, suitable techniques are required to reveal the orientation.

The classical tool of investigation, applicable in almost any case, of course is X-ray diffraction. It is perhaps less universally acknowledged that electron diffraction, which is feasible with most modern electron microscopes, may be used to advantage in this type of work, although the technique is described to some extent in several textbooks.[1] It is the purpose of the present paper to show how simply the orientation of a single crystal may be determined using reflexion electron diffraction, and what degree of precision may be attained. The method is exemplified by using a copper crystal, but it may be extended to other crystal systems.

METHOD

The single crystal is mounted in the diffraction stage of an electron microscope in such a way that its surface is parallel to the beam (Fig. 1). If it is then rotated around the surface normal, a number of different diffraction patterns will generally appear on the screen, depending both on the geometry and the crystal structure of the surface. All the patterns encountered during a rotation through 180° are recorded together with the corresponding angle of rotation. When they have been indexed, the surface normal and beam direction corre-
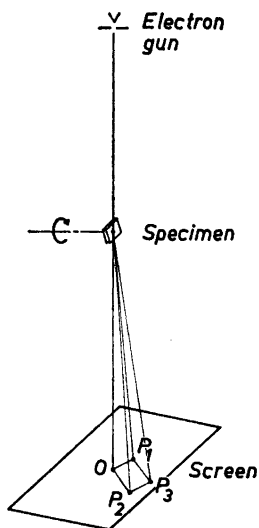
Fig. 1. Schematic drawing of the diffraction setup. O is the central spot and P_1, P_2, P_3 diffraction maxima. The specimen may be rotated around the axis indicated which is normal to its surface.

sponding to each setting may be calculated. Thus the orientation of the specimen with respect to the crystal lattice is determined from a number of different settings. From these results, average values of two directions, namely the surface normal and a reference direction in the surface may be computed, and the scatter of the individual measurements yields information concerning the experimental error.

Indexing procedure. The diagrams are conveniently indexed using the familiar Ewald construction in reciprocal space. The beam is made to pass through the origin of the reciprocal lattice (whose location is immaterial, whereas its orientation corresponds to that of the real crystal lattice). A sphere of radius $1/\lambda$ is constructed having its center in the beam direction and passing through the said origin. Diffraction maxima will then occur in directions going from the center of the sphere to all reciprocal lattice points situated on its periphery. In electron diffraction the sphere radius $1/\lambda$ is $10^1 - 10^2$ times greater than a typical distance $1/d_{hkl}$ between points in the reciprocal lattice. The small region of the sphere examined may therefore be replaced by a tangential plane. Another feature characteristic of electron diffraction is that, as a result of a number of factors, diffraction conditions are somewhat relaxed. This may conveniently be expressed by assigning finite dimensions to the reciprocal lattice points. The crystal may therefore be rocked slightly from its ideal orientation without the diagram disappearing, and sometimes reflexes belonging to two neighbouring but different orientations are found in one exposure.

The indexing is easily achieved if the following points are remembered.

1°. The diagram seen on the screen is simply an enlarged image of the intersection of the reciprocal lattice corresponding to the specimen with a plane perpendicular to the beam and passing through the origin. The directional relationship between direct and reciprocal lattice is maintained, so that if

the specimen is rotated through an angle the same applies to the reciprocal lattice. The magnification factor is $L\lambda$, where L is the camera length, and is best found by direct calibration.

2°. In the diagram, the beam impact point O is the origin of the reciprocal lattice. A reflex P situated at a distance $OP = R$ from the origin corresponds to a set of planes with spacing d_{hkl} where $R = L\lambda/d_{hkl}$. Spacings corresponding to low values of h, k, and l can be calculated, and the reflexes thus be identified by measuring distances of the type OP. In many cases, however, this procedure will give rise to a number of equivalent solutions because of crystal symmetry. For instance, a reflex from a cubic crystal corresponding to a spacing d_{hkl} may be assigned to any of the planes $(\pm h \pm k \pm l)$, $(\pm h \pm l \pm k)$, $(\pm k \pm h \pm l) \ldots$ so long as it is considered as an isolated phenomenon.

3°. If the diagram contains two reflexes P_1 and P_2 due to the planes $(h_1 k_1 l_1)$ and $(h_2 k_2 l_2)$, then the vector $\overline{P_1 P_2}$ must correspond to the plane $(h_2 - h_1 \ k_2 - k_1 \ l_2 - l_1)$, since $\overline{P_1 P_2} = \overline{P_1 O} + \overline{OP_2} = \overline{OP_2} - \overline{OP_1}$. This limits the number of combinations of indices for P_1 and P_2, if they are to be mutually consistent. Two reflexes P_1 and P_2 are often found to combine with O and a third reflex P_3 to form a parallelogram $OP_1P_3P_2$ where $\overline{OP_3} = \overline{OP_1} + \overline{OP_2}$ so that $h_3 = h_1 + h_2$ etc. The indexing of a diagram cannot be considered as correct unless the indices chosen are consistent with all the distances OP_i and P_iP_j.

4°. When indexing has been completed, the surface normal is drawn through O perpendicular to the shadow of the specimen surface. If a point P′ on this line can be indexed, its indices will be those of a lattice plane parallel to the specimen surface by virtue of the definition of the reciprocal lattice. The indexing is accomplished by intersecting the surface normal with a line joining two reflexes P_1 and P_2. If their intersection is P′, then

$$\overline{OP'} = \overline{OP_1} + \overline{P_1P'} = \overline{OP_1} + \frac{P_1P'}{P_1P_2} \overline{P_1P_2} = \overline{OP_1} + x\overline{P_1P_2}$$

and the indices of P′ will be $(h_1 + x(h_2 - h_1) \ k_1 + x(k_2 - k_1) \ l_1 + x(l_2 - l_1))$. In cases where all the planes causing reflexes are not in zone (see 5°), average values may be found using reflexes from both zones. When several patterns produced by the same crystal are indexed, the surface normal of course should have the same indices in each case. This is often a valuable help in combining the diagrams.

5°. All the planes whose reflexes are found in one diagram are in zone since their normals are all perpendicular to the beam direction. The latter may therefore be found from the vectorial product of any two normals $\overline{OP_1} \times \overline{OP_2}$. However, it has been mentioned that the reciprocal lattice points may be considered as having finite extension in space, and it may therefore happen that reflexes belonging to two planes of slightly different orientation are present in one diagram. In that case the beam direction may be given two different sets of indices. The averaging procedure described below may be used in such cases.

Example. To illustrate the above, let us consider the diagram reproduced in Fig. 2 which is a copy of an actual exposure of a copper crystal. The indices placed between bars have been calculated directly from measured distances
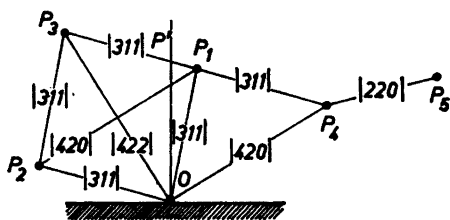
Fig. 2. Copy of a reflexion diffraction pattern obtained from a copper single crystal with a 75 kV electron beam. Figures between bars are possible indices corresponding to d_{hkl}-values found from measurements on the pattern.

of the type OP_i and P_iP_j, but their sign and order is arbitrary. As a starting point, reflex P_1 may be arbitrarily indexed (311). Considering next P_2, it follows from the diagram that its indices $(h_2k_2l_2)$ must satisfy two conditions, namely $|OP_2| = |h_2\ k_2\ l_2| = |311|$, and $|P_2P_1| = |3-h_2\ 1-k_2\ 1-l_2| = |420|$ if P_1 and P_2 are to be mutually consistent. The first condition admits any one of the solutions $(h_2k_2l_2) = (\pm3\ \pm1\ \pm1)$, $(\pm1\ \pm3\ \pm1)$ and $(\pm1\ \pm1\ \pm3)$; but only those which subtract from (311) to give $|420|$ will also satisfy the second. The possible combinations are readily surveyed in the following scheme:

$(h_1\ k_1\ l_1)$	3	1	1	3	1	1	3	1	1
$(h_2\ k_2\ l_2)$	±3	±1	±1	±1	±3	±1	±1	±1	±3
Difference	$\{0$	0	0	2	$\bar{2}$	0	2	0	$\bar{2}$
$(h_1-h_2\ \ k_1-k_2\ \ l_1-l_2)$	$\{6$	2	2	4	4	2	4	2	4

In the first case considered, the h-index of P_2P_1 may be either 0 or 6; k may be 0 or 2; and l may be 0 or 2 *etc.* Inspection of the scheme reveals that four solutions exist which all give $|P_1P_2| = |420|$. They are listed below together with other indices that follow directly:

$$\overline{OP_2} = \begin{cases}(\bar{1}31)\\(1\bar{3}1)\\(\bar{1}13)\\(11\bar{3})\end{cases} \quad \overline{P_2P_1} = \begin{cases}(4\bar{2}0)\\(240)\\(40\bar{2})\\(204)\end{cases} \quad \overline{OP_3} = \overline{OP_1} + \overline{OP_2} = \begin{cases}(242)\\(4\bar{2}2)\\(224)\\(42\bar{2})\end{cases} \quad \overline{OP_4} = \overline{P_2P_1}.$$

Each line gives one consistent set of solutions. The last reflex P_5 does not belong to the group considered since it cannot be reached by any combination of integer numbers of vectors such as $\overline{OP_1}$ and $\overline{OP_2}$. By treating the group OP_1P_5 alone in the way just described, possible indices are found to be $(6\bar{4}0)$ or $(60\bar{4})$. Since $|P_4P_5| = |220|$ it is clear that only two of the above four sets of solutions are consistent with P_5, namely the first row (with $6\bar{4}0$) and the third (with $60\bar{4}$). This completes the interpretation of reflexes.

The surface normal may be indexed by finding the vectorial components of its point of intersection P' with P_3P_1. Choosing the first set of solutions, one finds

$$\overline{OP'} = \overline{OP_1} + \frac{P_1P'}{P_1P_3}\ \overline{P_1P_3} = (3 + 0.20(-1) \quad 1 + 0.20 \times 3 \quad 1 + 0.20 \times 1)$$

$= (2.80\ 1.60\ 1.20)$. If P_5 were used in the construction, a slightly different orientation would be found for the surface normal.

The beam direction may be found using any pair of indices chosen from the consistent set of solutions. On the basis of (311) and ($\bar{1}$31) one finds

$$\begin{vmatrix} 1 & 1 \\ 3 & 1 \end{vmatrix} \quad - \begin{vmatrix} 3 & 1 \\ \bar{1} & 1 \end{vmatrix} \cdot \quad \begin{vmatrix} 3 & 1 \\ \bar{1} & 3 \end{vmatrix} = \bar{2}\ \bar{4}\ 10$$

or [12$\bar{5}$]; if (311) and (6$\bar{4}$0) are used, [2 3 $\bar{9}$]. An average may be computed using one of the methods described subsequently.

Averaging. When a number of diagrams, produced by the specimen in various positions around its surface normal, have been analyzed, average values may be calculated for the surface normal and a reference direction in the surface using the crystal axes as the coordinate system. Calculations are particularly easy when, as here, the lattice is cubic.

The average surface normal may be computed in either of two ways. The simplest consists in transforming each observed surface normal $[h_i k_i l_i]$ into the corresponding set of direction cosines $[\alpha_i \beta_i \gamma_i]$ by division with $(h_i^2 + k_i^2 + l_i^2)^{\frac{1}{2}}$, after which the average surface normal is obtained by addition as $[\sum \alpha_i \ \sum \beta_i \ \sum \gamma_i]$. The normalization ensures that all diagrams are weighted equally.

An alternative method is based on the beam directions found in the individual diagrams. If the beam were strictly perpendicular to the surface normal, then $\cos (\alpha_i \beta_i \gamma_i, \alpha \beta \gamma) = \alpha \alpha_i + \beta \beta_i + \gamma \gamma_i = 0$, where $\alpha_i \beta_i \gamma_i$ are the direction cosines of the i'th beam direction and $\alpha \beta \gamma$ those of the surface normal. In reality this is not so, but α, β and γ may be so chosen as to minimize the sum of squares of the deviations $\sum \cos^2 (\alpha \beta \gamma, \alpha_i \beta_i \gamma_i) = \sum (\alpha \alpha_i + \beta \beta_i + \gamma \gamma_i)^2$. α, β and γ may then be found by partial differentiation. However, α, β, and γ are interdependent, and calculations are simplified if they are replaced by a, b, and -1. Partial differentiation with respect to a and b and minimization then yield the two equations

$$a \sum \alpha_i^2 + b \sum \alpha_i \beta_i = \sum \alpha_i \gamma_i$$
$$a \sum \alpha_i \beta_i + b \sum \beta_i^2 = \sum \beta_i \gamma_i$$

from which a and b may be determined.

The other direction to be indexed in order to define the lattice position relative to the specimen geometry may conveniently be taken to be an arbitrary line in the surface (*e.g.* an engraved mark or an edge). Let the angle reading which indicates the degree of rotation of the specimen around its normal be v_r when the chosen reference direction with unknown indices $h_r k_r l_r$ coincides with the beam direction, and v_i when an indexed lattice direction $\alpha_i \beta_i \gamma_i$ is brought into the same position. Three equations then determine $\alpha_r \beta_r \gamma_r$:

$$\alpha_i \alpha_r + \beta_i \beta_r + \gamma_i \gamma_r = \cos (v_i - v_r)$$
$$\alpha_n \alpha_r + \beta_n \beta_r + \gamma_n \gamma_r = 0$$
$$\alpha_r^2 + \beta_r^2 + \gamma_r^2 = 1$$

where $\alpha_n \beta_n \gamma_n$ are the surface normal indices. Each diagram and its angular reading thus furnishes a set of indices, and an average set may be computed numerically.

Alternatively, a graphical method may be used. Let $\alpha_o \beta_o \gamma_o$ be the indices of an arbitrary direction in the surface, and v_o the corresponding angle. It is

then possible to calculate the angle $v_i - v_o$ between this direction and any beam direction $\alpha_i \beta_i \gamma_i$ with the corresponding setting v_i. If the calculated difference $v_i - v_o$ is plotted against v_i, a straight 45° line must result which can be used in transforming any measured angle v into $v - v_o$. When the (externally marked) reference direction is brought to coincide with the beam, as may be controlled optically, the corresponding angle reading v_r leads directly to the angle $v_r - v_o$ between the reference direction $\alpha_r \beta_r \gamma_r$ and the lattice direction $\alpha_o \beta_o \gamma_o$ from which the former may be found.

EXPERIMENTAL

A piece of copper approximately $8 \times 6 \times 1$ mm was cut out of a flat large copper single crystal of the same thickness, prepared from 99.999 % copper by high vacuum melting in a graphite mould. It was electropolished in a 1000 g/l H_3PO_4 solution at 1.8 V for 30 min to smoothen the surface and remove strained metal, etched electrolytically in the same bath at 0.7 V for 2 min, thoroughly rinsed in distilled water and finally blown dry in a jet of purified CO_2. This treatment ensures that the surface is clean, undistorted and sufficiently rough to give a reasonably sharp pattern of the transmission type, even at glancing angles of incidence.

The copper plate was then mounted with Aquadag graphite suspension on a specimen holder, its surface being normal to the rotational axis of the latter, and placed in the diffraction stage of a HU 11A Hitachi electron microscope (camera length 445 mm, negative size 52×80 mm). The surface was oriented optically so as to be parallel to the (vertical) beam, and the angle of rotation around its normal was measured on the holder with a precision of about 1°. The following microscope settings were used with satisfactory results: HV 75 kV; wide bore pole piece and no current in projection lens; objective lens at its lowest current setting; intermediate lens adjusted to focus the central spot on the screen; condensor lenses set to give maximum brightness; condensor aperture 300 μ; objective aperture (centered on the intermediate lens axis) 200 μ; selected area aperture brought to coincide with the objective aperture on the screen. The specimen was rotated through 180° about its normal, and each set of reflexes encountered was photographed. The exposures were enlarged $3 \times$ in a printing apparatus before indexing.

Table 1. Direction cosines of surface normal determined from 11 settings of crystal; squares of cosine deviations from average, and angular deviations from average.

Exposure No.	Surface normal			Squares of deviations $\times 10^8$				Angular deviation Θ_i from average normal (°)
	α_i	β_i	γ_i	$(\alpha_i - \overline{\alpha})^2$	$(\beta_i - \overline{\beta})^2$	$(\gamma_i - \overline{\gamma})^2$	Sum	
1	0.7862	0.4984	0.3653	53 361	106 276	5 476	165 113	2.33
2	0.8132	0.4698	0.3434	1 521	1 600	21 025	24 146	0.89
3	0.8003	0.4847	0.3529	8 100	35 721	2 500	46 321	1.23
4	0.7976	0.4730	0.3741	13 689	5 184	26 244	45 117	1.22
5	0.7905	0.4679	0.3952	35 344	441	139 129	174 914	2.40
6	0.8167	0.4427	0.3700	5 476	53 361	14 641	73 478	1.55
7	0.8261	0.4618	0.3230	28 224	1 600	121 801	151 625	2.23
8	0.8193	0.4567	0.3466	10 000	8 281	12 769	31 050	1.01
9	0.8154	0.4542	0.3588	3 721	13 456	81	17 258	0.75
10	0.7998	0.5147	0.3088	9 025	239 121	241 081	489 227	4.01
11	0.8292	0.3952	0.3952	39 601	498 436	139 129	677 166	4.72
Sum	8.8943	5.1191	3.9333	208 062	963 477	723 876	1 895 415	22.34

RESULTS

Following the description given above, eleven diffractograms were obtained and indexed. The surface normals, as calculated from the diagrams and subsequently reduced to direction cosines $\alpha_i\beta_i\gamma_i$ are listed in Table 1. The average surface normal $[\bar{\alpha}\bar{\beta}\bar{\gamma}]$ is found by normalization of the sum vector $\sum \alpha_i \sum \beta_i \sum \gamma_i$ to be [0.8093 0.4658 0.3579]. The error of each of the three components in a single measurement may be estimated from sums of the type $\sum(\alpha_i-\bar{\alpha})^2$ to be 0.0144; 0.0310; and 0.0269 corresponding to 1.4°; 2.0°; and 1.7°. Or the angular deviation Θ_i between the individual normal $\alpha_i\beta_i\gamma_i$ and the average direction $\bar{\alpha}\bar{\beta}\bar{\gamma}$ may be found directly since

$$\Theta_i \simeq 2\sin\frac{\Theta_i}{2}=[(\alpha_i-\bar{\alpha})^2+(\beta_i-\bar{\beta})^2+(\gamma_i-\bar{\gamma})^2]^{\frac{1}{2}}$$

This has been done in the table, and it will be seen that the average error of a single measurement is about 2°, so that the probable error of the average direction is rather less than 1°.

These results agree reasonably well with the surface normal direction obtained from the criterion that it should be as nearly perpendicular to all the beam directions as possible. Using the method already described one finds the surface normal to be [0.7993 0.4775 0.3649].

The beam directions calculated from the same eleven diffractograms, and similarly reduced to direction cosines, are given in Table 2. In order to test their consistency, the angles v_i-v_0 between the beam direction $\alpha_i\beta_i\gamma_i$ and a fixed direction $\alpha_0\beta_0\gamma_0$ in the surface have been calculated. The latter direction, $\alpha_0\beta_0\gamma_0$, which is arbitrary, has been chosen to be [0.5841 −0.5739 −0.5739] in an attempt to give equal weight to α_i, β_i and γ_i in a convenient way. The last column contains the angles of specimen orientation as measured on the specimen holder for each diffractogram. The difference $v_{i,obs}-(v_i-v_0)_{calc}$ should be constant; its average value is 6.1° with an uncertainty of 1.8° on a

Table 2. Direction cosines of beam for 11 settings of crystal; calculated angle between beam direction and [0.5841 −0.5739 −0.5739], observed setting angle of crystal, and difference between these (°).

| Exposure No.	Beam direction			$\cos(v_i-v_0)_{calc}$	$(v_i-v_0)_{calc}$	$v_{i,obs}$	$v_{i,obs}-(v_i-v_0)_{calc}$
	α_i	β_i	γ_i				
1	0.5883	−0.7845	−0.1961	0.9064	−25.0	−22	3.0
2	0.5773	−0.5773	−0.5773	0.9998	+ 1.1	+ 6	4.9
3	0.5651	−0.4139	−0.7137	0.9772	12.3	17	4.7
4	0.5345	−0.2672	−0.8018	0.9256	22.2	29	6.8
5	0.4472	0	−0.8944	0.7745	39.2	46	6.8
6	0.2789	0.2200	−0.9348	0.5731	55.0	62	7.0
7	0.2370	0.2715	−0.9329	0.5180	58.8	67	8.2
8	0.1934	0.3364	−0.9217	0.4489	63.3	71	7.7
9	0.1974	0.3556	−0.9136	0.4355	64.2	72	7.8
10	0	0.5145	−0.8575	0.1968	78.6	82	3.4
11	0	0.7071	−0.7071	0	90.0	97	7.0
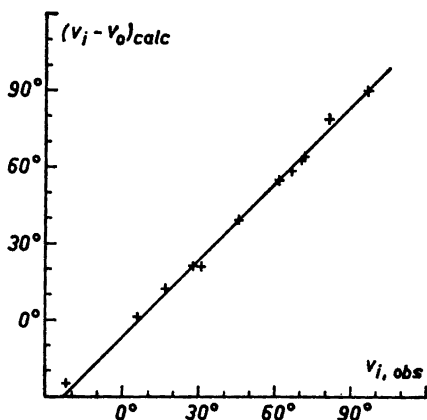
Fig. 3. Plot of $(v_i - v_o)_{\text{calc}}$ *vs.* $v_{i,\text{obs}}$. The former is the angle between the beam direction in the i'th setting, calculated from the diffraction pattern, and an arbitrary fixed direction in the surface [0.5841 −0.5739 −0.5739]; and the latter is the corresponding angle of rotation measured on the specimen holder.

single measurement and 0.5° on the average value. The results are shown in Fig. 3 where $(v_i - v_o)_{\text{calc}}$ has been plotted against $v_{i,\text{obs}}$.

It may be mentioned that the growth direction $\alpha\beta\gamma$ of the single crystal, which coincided with the beam direction at a setting of $v_r = 70°$, was calculated to be [0.2014 0.3524 −0.9139] from the following equations: (1) $0.8093\alpha + 0.4658\beta + 0.3579\gamma = 0$; (2) $0.5841\alpha - 0.5739\beta - 0.5739\gamma = \cos(70° - 6.1°)$; (3) $\alpha^2 + \beta^2 + \gamma^2 = 1$.

From general experience, illustrated by the above cited example, it may be inferred that high resolution electron diffraction, which can be undertaken with most types of electron microscopes, constitutes a valuable tool in the determination of the orientation of a crystal lattice. Exposure times are short, indexing of the diffractograms is a relatively simple matter, and the precision attained — of the order of 2° on a single measurement — is sufficient in most applications.

It should be added that all the measurements mentioned were carried out using standard equipment, and that no extreme care was taken in preparing the specimen surface. However, the state of the latter is of great importance, particularly in reflexion type geometry where it is essential that the surface be clean, and that the undistorted lattice extend right to the boundary. Furthermore, poor resolution is encountered when specimens having a very flat surface are examined. In such cases a relatively large number of diagrams will be found with a corresponding loss in precision. Where high resolution is obtained, due to a rough surface giving a transmission type pattern, the specimen orientation relative to the beam direction is critical; and few, if any, diagrams will be found. Between the two extremes exists a broad range where the method described may be employed advantageously.

REFERENCES

1. See, *e.g.*, Thomson, G. P. and Cochrane, W. *Theory and Practice of Electron Diffraction,* Macmillan, London 1939; Pinsker, Z. F. *Electron Diffraction,* Butterworth, London 1953.