11.3 The analysis of electron diffraction patterns

The analysis of electron diffraction patterns is essentially a process of identifying the reciprocal lattice sections which give rise to them. Several computer programs are now available (see Appendix 1) which generate reciprocal lattice sections, given as input data the lattice parameters, type of unit cell (and in some cases the space group and atomic positions) and the electron beam (zone axis) direction. Several examples showing the ZOLZ only are given in Fig. 11.3. Care must be exercised in using such data because a number of different electron diffraction patterns from different types of high-symmetry crystals have identical symmetry and only differ in scale. For example the \( \langle 111 \rangle _{fcc} \) and \([000l]_{hcp}\) patterns shown in Figs 11.3(b) and (d) both consist of hexagonal patterns of points.

The first step in the analysis of electron diffraction patterns is measurement of the \( d \)-spacings. This is an easy matter. Figure 11.4 shows a set of reflecting planes at the Bragg angle \( \theta \) (much exaggerated) to the electron beam. The diffracted beam, at angle \( \theta + \theta = 2\theta \), to the direct beam, falls on the screen at a distance \( R \) from the centre spot. Figure 11.4 does not represent the actual ray paths in the electron microscope, which are of course determined and controlled by the lens settings: hence \( L \), the camera length, is not the actual distance between the specimen and screen, but is a ‘projected’ distance which varies with the lens settings.

From Fig. 11.4, \( \tan 2\theta = R/L \). Since \( \theta \) is small, \( \tan 2\theta \approx 2\theta \) (2\( \theta \) of course being measured in radians). Similarly for Bragg’s law, \( \sin \theta \approx \theta \) hence \( \lambda \approx 2d_{hkl}\theta \). Eliminating \( \theta \) from these equations we have:

\[
d_{hkl} = \lambda L/R
\]

where \( \lambda L \) is known as the camera constant and which, like \( L \), varies with lens settings in the microscope. The units of \( \lambda L \) are best expressed in terms of the product of \( R \), the distance measured on the screen (e.g. mm) and \( d_{hkl} \) (e.g. nm, Å or pm). Although the
Fig. 11.3. Examples of the computer-generated diffraction patterns, drawn to the same scale ($\lambda L = 16.1 \text{ Å mm}$). (a) Aluminium (fcc), zone axis = $\langle 110 \rangle$; (b) aluminium (fcc), zone axis = $\langle 111 \rangle$; (c) iron (bcc), zone axis = $\langle 112 \rangle$; (d) titanium (hcp), zone axis = $[0001]$. Ångström (Å) is not an SI (Système International) unit, it is coherent with the SI system ($1 \text{ Å} = 10^{-10} \text{ m}$) and still remains in widespread use in crystallography (a) because it is roughly equal to atomic diameters and (b) because X-ray $d_{hkl}$-spacing data in the Powder Diffraction File (see Section 10.3) is recorded in ångströms.

The accuracy with which the $d_{hkl}$-spacings can be measured is very limited because of the size or ‘diffuseness’ of the diffraction spots. Moreover the camera constant, $\lambda L$, will only be known to a high degree of accuracy if a ‘standard’ specimen is used which gives a diffraction pattern with spots of accurately known $d_{hkl}$-spacings. Otherwise the small variations in lens settings from specimen to specimen and from day-to-day will limit the accuracy of $\lambda L$ values at best to three significant figures. Hence, as pointed out above, patterns which have identical symmetry but which only differ slightly in scale with respect to the $d_{hkl}$-spacings of the diffraction spots are not readily distinguished.

The spots may then be indexed by reference to tables of data such as are contained in the Powder Diffraction File, which show the (Laue) indices, $hkl$, corresponding to...
the measured $d_{hkl}$-spacings. In doing so, a further step is required: the indexing must be such that the addition rule (Section 6.5.2) is satisfied. A given set or family of planes \{hkl\} (which are invariably listed in data files simply as hkl—no brackets) will consist of a number of variants of identical $d_{hkl}$-spacings. For example, in the cubic system (see Section 5.4), there are six variants of the ‘plane of the form’ \{100\}, all of which have identical $d_{hkl}$-spacings. The procedure consists of choosing the appropriate variants such that the addition rule is satisfied. Consider, for example, Fig. 11.3(a). The four spots of identical $d_{hkl}$-spacings closest to the centre spot are all reflections from planes of the form \{111\}. The particular indices have been chosen such that the indices of the remaining spots are determined correctly. For example, $d_{111}^* + d_{002}^* = d_{101}^*$ and the zone axis, [110], is found by cross-multiplication of any pair of these indices (see Sections 5.6.2 and 6.5.7), the ‘choice’ only needs to be made once, and having been made, all the other spots in the pattern can be indexed consistently by repeated application of the addition rule; again, with reference to Fig. 11.3(a), $d_{111}^* + d_{002}^* = d_{113}^*$ and so on. The ‘choice’ is of course arbitrary: the number of different choices which can be made, all leading to a self-consistently indexed diffraction pattern, depends on the number of equivalent variants of the zone axis. In a cubic crystal there are twelve variants of the (110) direction, hence there are twelve ways in which a pattern like that of Fig. 11.3(a) can be indexed.

The availability of computer-generated diffraction patterns has greatly facilitated the indexing and verification of electron diffraction pattern analysis. However, it must
be said that many ‘useful’ diffraction patterns—i.e. those which may be of potential scientific interest, which have been obtained under conditions of experimental difficulty and which may consist of many spots from several crystals of varying degrees of visibility on the film—still require for their solution careful observation and measurement and an awareness of the possible occurrence of additional complicating factors such as double diffraction (see Appendix 6). Those books on electron diffraction techniques in Further reading provide a more detailed and thorough coverage of these topics.

11.4 Applications of electron diffraction

11.4.1 Determining orientation relationships between crystals

One of the greatest advantages of electron diffraction is the facility in the electron microscope of being able to select a particular area of the specimen and to vary the diameter of the beam to obtain diffraction patterns simultaneously from those phases of interest. Moreover, the reflections from the phases present may be distinguished by the technique of dark field imaging. Each electron diffraction pattern may be indexed according to the procedures described in Section 11.3. The orientation relationship(s) may then be given in terms of parallelisms between zone axes and planes.

Figure 11.5(a) shows an electron diffraction pattern of $\alpha$-iron $a = 2.866$ Å (bcc—strong reflections) in which are precipitated (or exsolved) particles of Fe$_2$TiSi, $a = 5.732$ Å (fcc—weak reflections) in a single crystallographic orientation. It is obvious, simply by inspection or looking, that there is a clearly defined orientation relationship between the iron matrix and the precipitate and, because of the coincidence of many of the
reflections, that the lattice parameters are related in some rational ratio. The \( d \)-spacings of the reflections may be measured (Section 11.3) and, given the lattice parameters and the conditions for reflection for the cubic \( F \) (fcc) and cubic \( I \) (bcc) lattices (Table A6.2), the reflections may be indexed. Figure 11.5(b) shows the patterns indexed according to one (arbitrary) variant of the orientation relationship. Note that the 200 Fe\(_2\)TiSi spot is half the distance (and therefore twice the \( d \)-spacing) of the 200 \( \alpha \)-Fe spot from the centre; these planes are therefore parallel and the lattice parameter of Fe\(_2\)TiSi is twice that of \( \alpha \)-Fe. Similarly, the 022 Fe\(_2\)TiSi reflection (by vector addition of \( \bar{1}11 \) and 111) is coincident with 011 \( \alpha \)-Ti. The zone axes, obtained by cross-multiplication (Section 11.3), are both [0\( \bar{1}1 \)]\(^1\). The orientation relationship may be specified by quoting the parallelisms:

\[
(200)_{\text{Fe}_2\text{TiSi}} \parallel (200)_{\alpha \text{-Fe}} \\
[011]_{\text{Fe}_2\text{TiSi}} \parallel [011]_{\alpha \text{-Fe}}.
\]

This is known as the ‘cube-cube’ orientation relationship because it is equivalent to the statement that the \( x \), \( y \), \( z \) axes of both crystals are mutually parallel.

Other, more complicated, orientation relationships may be determined by the same simple approach, but to go from the parallelisms between the planes and zone axes observed for the particular patterns to the establishment of possible parallelisms between planes not observed in the patterns (i.e. those that are not (nearly) parallel to the electron beam direction), requires a knowledge of the stereographic projection (see Chapter 12).

### 11.4.2 Identification of polycrystalline materials

The Powder Diffraction File may be used to identify polycrystalline specimens from their electron diffraction patterns. However, its use is much more limited owing to the fact that the \( d \)-spacings of the diffraction rings can be measured to a much lower level of accuracy and only qualitative estimates can be made of their relative intensities. Hence the use of search procedures, as described in Section 10.3.2, is uncommon. Usually we have a fair idea as to what the specimen might be and make direct comparisons between the experimental data and that of ‘possible’ patterns in the File. Exercise 11.4 gives an example of this in the case of a single-crystal electron diffraction pattern.

Figure 11.6 gives an example of an electron diffraction ‘ring’ pattern from a fine-grained polycrystalline thin foil specimen of aluminium. It is, in effect, the superposition of many single-crystal patterns. Notice the variations in intensity and the sequence of spacings of the rings. Aluminium can immediately be recognized as having the fcc structure since the rings occur in the characteristic sequence ‘two-together’, ‘one-on-its-own’, ‘two-together’, etc. (see Note 3, Table A6.2). Hence the rings may simply be indexed ‘by inspection’, i.e.

\[
111, 200, \quad 220, \quad 311, 222, \quad 400, \quad 331, 420.
\]

\(^1\) The order of cross-multiplication is important; one should read anticlockwise. E.g. for the \( \alpha \)-iron diffraction spots write down (211) as the first line in the memogram and then (011) as the second line. This gives (for the usual right-handed axial system) the zone axis direction upwards (i.e. anti-parallel to the electron beam which is much easier to deal with when plotting the data on a stereographic projection (Chapter 12)).
11.4.3 Identification of quasiperiodic crystals

In Section 4.8 we showed how quasiperiodic crystals or crystalloids could nucleate and grow without any long range translational symmetry and that their existence was first recognised from the ten-fold symmetry of their electron diffraction patterns. Figure 11.7 shows the first observed such electron diffraction pattern of a nodule-like phase in a rapidly quenched Al-25 wt.% Mn alloy. Such a ten-fold pattern does not however constitute sufficient evidence for quasiperiodicity since multiply-twinned crystals (consisting of 10 twin-related segments radiating out from a central point rather like the slices of a cake) can also give rise to such ten-fold patterns. Nor is this a remote possibility and some alloy systems may exhibit quasiperiodic crystals or multiply-twinned crystals (the microcrystalline state) depending upon heat treatment. For example the Al_{65}Cu_{20}Fe_{15} alloy gives twinned microcrystals when slowly cooled from the melt which on heating transform to quasiperiodic crystals.

There are two ways in which these quasiperiodic and multiply-twinned states may be distinguished. First the evidence from microscopy: twin boundaries and the changes in orientation of lattice fringes at twin boundaries may be observed by high resolution electron microscopy—which constitutes firm evidence for the microcrystalline phase. Second, the fine detail of the spots in the electron diffraction patterns: the segments or ‘slices of cake’ in multiply-twinned crystals are not perfectly related by five-fold

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symmetry; there is some misalignment which results in spots of a triangular 'shape' (i.e. made up of a group of little sub-spots) rather than the clear and distinct single spots of Fig. 11.7. Other, more complicated five-fold patterns of spots may also arise. It is not surprising that the first reported occurrences of quasiperiodic crystals were greeted with considerable scepticism throughout much of the crystallographic community.

11.5 Kikuchi and electron backscattered diffraction (EBSD) patterns

11.5.1 Kikuchi patterns in the TEM

We first consider the trajectories, or paths, of the inelastically scattered electrons within the specimen (Section 11.1). These occur over a range of angles, the scattering being most intense at small angles to the incident beam and decreasing at larger angles, giving in effect a 'pear-shaped' distribution of intensity as shown schematically in the upper part of Fig. 11.8. This distribution of intensity around the incident electron beam (the centre spot) is shown in the lower part of Fig. 11.8. Such a distribution is only observed in practice in 'thicker' specimens (in the range 200 nm upwards) and in which the amount of inelastic scattering is significant. It is almost entirely absent in the thin foil specimens from which the electron diffraction patterns shown in Figs 11.5(a), 11.17, 11.18 and 11.19 were obtained.

Now we describe the elastic scattering, or Bragg reflection, of the weakly inelastically scattered electrons that have suffered negligible changes in wavelength. Consider a specimen in which a set of $hkl$ planes is at an angle to the incident beam slightly smaller