5. DETERMINATION OF LATTICE PARAMETERS

5.3.3.4.3.4. *Advantages and disadvantages of the Bond method*

The significant advantages of the Bond (1960) method, such as:

(*a*) very high accuracy;

(*b*) rather high precision;

(*c*) well elaborated analysis of errors;

(*d*) a simple arrangement, which may be realized on the basis of a standard diffractometer with computer control and, if necessary, supplemented with suitable attachment; and

(*e*) variety of applications;

make this method one of the most popular at present.

The method, however, has the following limitations:

(i) Special requirements concerning the sample are difficult to satisfy in some cases.

(ii) Problems arise with determination of all the lattice parameters of non-cubic crystals. Multiple-sample preparation or a special approach is needed in such cases.

(iii) Lattice-spacing determination from small spherical crystals requires additional corrections or fourfold measurements.

(iv) Displacement of the irradiated area on the sample surface (Wołcyrz, Pietraszko & Łukaszewicz, 1980; Berger, 1984) complicates examination of the real structure (for example, by local measurements).

(v) The method is rather time-consuming, since twofold scanning of the profile is required for determination of a single θ value.

(vi) Because two detectors, or a wide range of rotations of only one detector, are required, measurement with additional attachments is more difficult than on an asymmetric diffractometer.

Nevertheless, the geometry proposed by Bond (1960), owing to its advantages, is commonly used in precise and accurate multiple-crystal spectrometer methods (§§5.3.3.7.1, 5.3.3.7.2).

Other limitations concerning the precision and accuracy of the method are common to it and to all the 'traditional' methods (Subsection 5.3.3.5).

5.3.3.5. *Limitations of traditional methods*

As 'traditional' are considered the methods that depend on a comparison of the lattice spacings to be determined with the wavelength values of characteristic X-radiation that comes directly from laboratory (*Bremsstrahlung*) sources. The *emission lines* are *wide and asymmetric*, which limits both the accuracy and precision of lattice-parameter measurements (as discussed in Subsection 5.3.1.1). One of the limiting factors is the *uncertainty of the wavelength value*. For many years, the wavelength values determined by Bearden (1965, 1967) with an accuracy of 5 parts in 10^6 were widely used. At present, owing to remarkable progress in the measurement technique, it is possible to achieve an accuracy in wavelength of an order better, and nowadays remeasurements of some characteristic emission X-ray wavelengths are reported [*cf.* §5.3.3.3.1(iii) and Subsection 5.3.3.8]. Yet, even after reducing the uncertainty in wavelength, and after introducing all necessary corrections for systematic errors, the highest accuracy of traditional methods does not exceed 1 part in 10^6 (*cf.* Subsection 5.3.3.8).

The accuracy of an order better is possible with X-ray and optical interferometry. This *non-dispersive method (cf.* Subsection 5.3.3.8) is used for accurate lattice-spacing determination of highly perfect standard crystals; the standards are next used for both lattice-parameter determination with a double-beam comparison technique (Baker & Hart, 1975; see also

§5.3.3.7.3) and for the accurate wavelength determination mentioned above.

Another problem is the limited precision attainable by traditional methods. As was discussed in Subsection 5.3.1.1, the width of the diffraction profile depends on the spectral distribution of the wavelength, (5.3.1.6), (5.3.1.7), (5.3.1.8), and cannot be less than this owing to the wavelength dispersion. However, much has been done to approach this limit and to attain the precision and accuracy of the diffraction profile location (*cf.* Subsection 5.3.3.3). The highest precision of lattice-parameter determination that it is possible to achieve with traditional methods is about 1 part in 10^7. For some problems connected with single-crystal characterization, such as the effect of irradiation, stress, defect concentration, including local measurement (topography), better precision is required.

From (5.3.1.9), the other possibility of increasing precision, besides choosing optimum parameters for the measurement and improvement of profile-location methods, is to influence the original profile $h_\lambda(\omega)$. This aim can be attained either by applying spectrally narrower X-ray sources or by reducing the width of the original profile by means of arrangements with additional crystals playing the role of monochromator and reference crystal. This second possibility is applied in double- or triple-crystal spectrometry, in multiple-beam methods, or in combined methods. These methods are called '*pseudo-non-dispersive*' methods, since the width of the diffraction profile is considerably limited in them owing to considerable limitation of the width of the original profile. A similar situation to that in n-crystal spectrometers, in which the beam reflected from one set of crystal planes is the source of radiation for the second (or the next) diffraction phenomena, arises in multiple-diffraction methods; this is described in Subsection 5.3.3.6.

A systematic and well illustrated review of pseudo-non-dispersive and other differential methods is given by Hart (1981), who is the author of numerous papers on this subject.

5.3.3.6. *Multiple-diffraction methods*

Multiple diffraction occurs when two or more sets of planes simultaneously satisfy the Bragg law for a single wavelength λ. The beam diffracted from one set of planes becomes the incident beam within the crystal for the next diffraction. In the reciprocal-space representation, this means that three or more reciprocal-lattice points lie simultaneously on the Ewald sphere (Fig. 5.3.3.5). These points can be detected by successive rotations of the crystal, as described below. This phenomenon, known also as
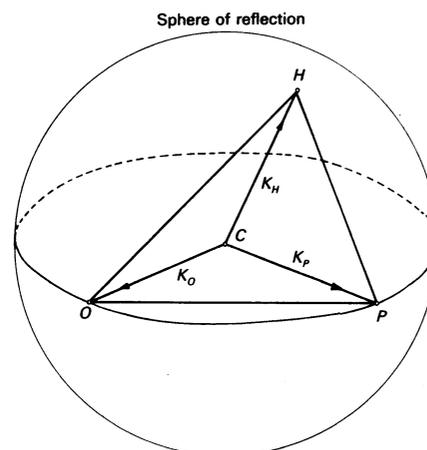

Fig. 5.3.3.5. Schematic representation of multiple diffraction in reciprocal space (after Post, 1975).

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