

## 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 (Wołczyrz, 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  $\theta$  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  $h_i(\omega)$ . 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  $\lambda$ . 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

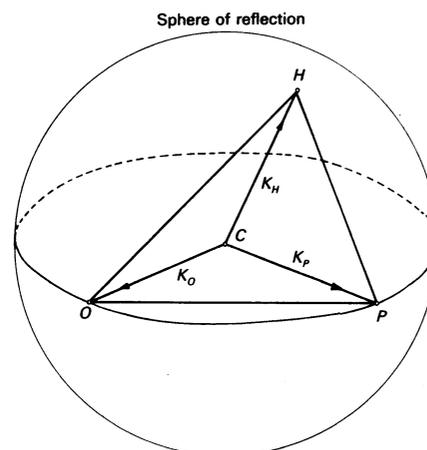


Fig. 5.3.3.5. Schematic representation of multiple diffraction in reciprocal space (after Post, 1975).

### 5.3. X-RAY DIFFRACTION METHODS: SINGLE CRYSTAL

simultaneous reflection or (after Renninger, 1937) 'Umweganregung', may be observed in both X-ray and neutron experiments. In the first case, it occurs both in methods with counter recording, initiated by Renninger (1937), and in methods with photographic recording in which a highly divergent beam is used (§5.3.2.4.2). The intersections of conic sections encountered in the methods developed by Kossel (1936) and Lonsdale (1947) are the cases of multiple-diffraction phenomena in photographic methods.

Simultaneous reflection, undesirable in some cases ('forbidden' reflections in measurements of intensities) can be very useful in others. Its various applications have been reviewed by Terminasov & Tuzov (1964) and Chang (1984). Only the utility of multiple diffraction in lattice-parameter determination will be discussed here.

The principle of Renninger's (1937) experiment, which is also the basis of the method described by Post (1975), is shown in Fig. 5.3.3.6. The crystal in the shape of a slab is at first set in a position to diffract the primary X-ray beam. A primary reflection whose intensity is very low or which is forbidden by the space group of the crystal is usually selected. Its intensity determines the background intensity of the pattern, which should be low. The detector, with a wide-open window, is situated in the appropriate position and remains fixed throughout the experiment while the crystal is rotated around the axis perpendicular to the crystal planes (and its surface) to record successive reflections.

The multiple-diffraction pattern (an example is shown in Fig. 5.3.3.7) has next to be indexed. The principle of the method of indexing, known as the reference-vector method (Cole, Chambers & Dunn, 1962; Post, 1975; Chang, 1984), is shown in Fig. 5.3.3.6(b). Directions of the primary and diffracted beams are marked by vectors  $\mathbf{K}_0$  and  $\mathbf{K}$ . The ends of the vectors lie on the Ewald sphere, the radius of which is equal to  $1/\lambda$ . The reciprocal vector  $\mathbf{P} = h_0\mathbf{a}^* + k_0\mathbf{b}^* + l_0\mathbf{c}^*$ , being the difference between the vectors  $\mathbf{K}$  and  $\mathbf{K}_0$ , represents the first diffraction phenomenon, which is observed for setting angles equal to  $\varphi_0$  and  $\mu$  (usually  $\mu = \theta$ ). Let us assume that the reciprocal vector  $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ , observed for setting angles  $\varphi_0 + \beta$  and  $\nu$ , represents the next diffraction. The vector components of  $\mathbf{H}$ , parallel and normal to  $\mathbf{P}$ , are denoted by  $\mathbf{H}_p$  and  $\mathbf{H}_n$ , respectively. For a given wavelength, the lengths  $P, H, H_p, H_n$  of respective vectors  $\mathbf{P}, \mathbf{H}, \mathbf{H}_p, \mathbf{H}_n$  are functions of lattice parameters and diffraction indices.

The task is to find the relationship between the difference  $\beta$  of angles of rotation (or between two values of the setting angles,  $\beta$  and  $\nu$ ) and the lengths of the reciprocal vectors. The following relations result from Fig. 5.3.3.6(b):

$$\cos \beta = \frac{(C'A')^2 + H_n^2 - R^2}{2H_n(C'A')},$$

$$(C'A')^2 = R^2 - P^2/4,$$

$$H_p = P/2 - R \sin \nu,$$

$$R' = R \cos \nu.$$

Taking these into consideration, and remembering that  $H^2 = H_p^2 + H_n^2$ , we finally obtain

$$\cos \beta = \frac{H^2 - H_p P}{2H_n(R^2 - P^2/4)^{1/2}}. \quad (5.3.3.34)$$

Since  $\cos(-\beta) = \cos \beta$ , the appearance of successive reflections does not depend on the direction of rotation. A detailed discussion of (5.3.3.34) is given by Cole, Chambers & Dunn (1962) and Chang (1984). When preliminary values of the lattice parameters are known, (5.3.3.34) can be applied for indexing multiple-diffraction patterns. A computer program (Rossmannith, 1985) can be very useful in rather complicated calculations and in the graphical representation of the multiple-diffraction

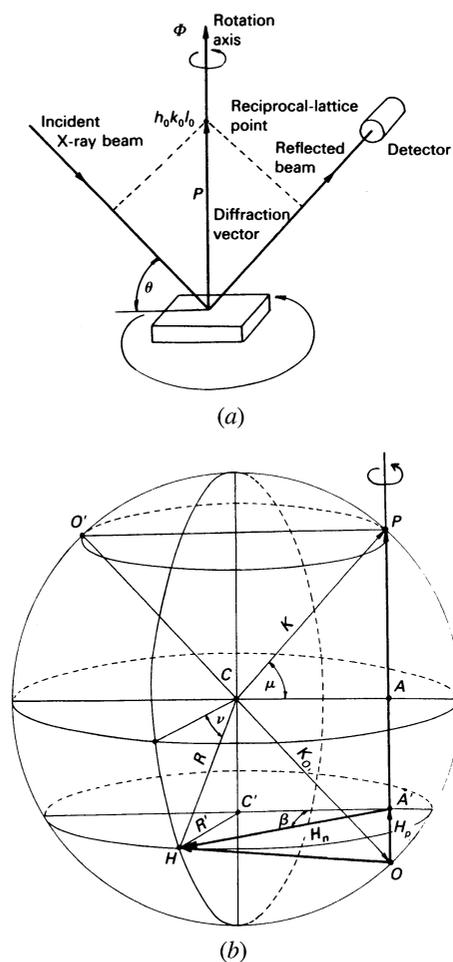


Fig. 5.3.3.6. Schematic representation of the multiple-diffraction method. (a) Experimental set-up (after Cole, Chambers & Dunn, 1962; Post, 1975). (b) Geometric representation in reciprocal space.

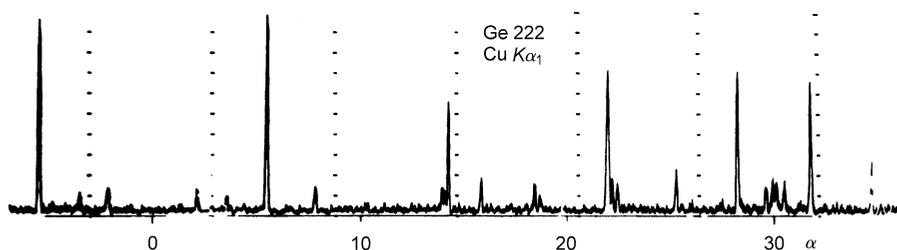


Fig. 5.3.3.7. The multiple-diffraction pattern at the 222 position in germanium (Cole, Chambers & Dunn, 1962).

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pattern. Formula (5.3.3.34), since  $C'A' = R \cos \mu$ , can be presented in another form:

$$R = \frac{H^2 - H_p P}{2H_n \cos \mu \cos \beta}, \quad (5.3.3.35)$$

where two setting angles,  $\mu$  and  $\beta$ , are taken into account. When the indices are known, both (5.3.3.34) and (5.3.3.35) can be used for the determination or refinement of lattice parameters.

Another analytical method for indexing multiple-diffraction patterns, based on the determination of the Lorentz point, has been described by Kshevetsky, Mikhailyuk, Ostapovich, Polyak, Remenyuk & Fomin (1979).

Formulae (5.3.3.34) and (5.3.3.35) are valid for all crystal systems. In practice, however, the rather complicated method is used mainly for cubic crystals, and a special approach proved to be needed in order to adapt the method to other (rectangular) systems (Kshevetsky, Mikhalychenko, Stetsko & Shelud'ko, 1985). In the case of a cubic lattice, it is convenient to substitute

$$R = a/\lambda \quad (5.3.3.35a)$$

into (5.3.3.34) and (5.3.3.35) rather than  $R = 1/\lambda$  used in the general case, so that the lengths of the reciprocal vectors, being now functions of the indices only, are:

$$P = (h_0^2 + k_0^2 + l_0^2)^{1/2}, \quad (5.3.3.35b)$$

$$H = (h^2 + k^2 + l^2)^{1/2}, \quad (5.3.3.35c)$$

$$H_p P = \mathbf{HP} = h_0 h + k_0 k + l_0 l. \quad (5.3.3.35d)$$

The lengths of the components of  $\mathbf{H}$  can be determined from (5.3.3.35b,c,d) taking  $H_p = H_p P/P$  and  $H_n = (H^2 - H_p^2)^{1/2}$ . After introducing the alterations [equation (5.3.3.35a) and the resulting equations (5.3.3.35b,c,d)], (5.3.3.35) now describes a simple dependence between the ratio  $a/\lambda$ , the indices, and the setting angles.

The accuracy of the lattice-parameter determination resulting from (5.3.3.35) in the cubic case can be assumed to be:

$$\frac{\Delta a}{a} = \tan \mu \Delta \mu + \tan \beta \Delta \beta; \quad (5.3.3.36)$$

this thus depends on the values of the setting angles  $\beta$ ,  $\mu$  and their accuracies  $\Delta \beta$ ,  $\Delta \mu$ . The latter depend on various systematic errors.

Since the differences between the two angular settings at which a given set of planes diffracts are measured rather than their absolute values, the systematic errors due to absorption, specimen displacement, and zero-setting are eliminated. In contrast, errors due to vertical divergence, refraction and the change of wavelength of the incident radiation (when it enters the crystal), alignment, and dynamical effects should be taken into account. In the case described by Post (1975), when a fine focus (effective size  $0.4 \times 0.5$  mm) and collimation limiting the beam divergence to  $2'$  were used, the vertical divergence causing the relative error in  $d$  of about  $5 \times 10^{-8}$  could be ignored.

The errors due to the real structure (inhomogeneity, mosaicity and internal stress) were discussed by Kshevetsky *et al.* (1979).

The accuracy possible by this method (from 1 to 4 parts in  $10^6$ ) is comparable with that obtained with the Bond (1960) method. The advantages of this method from the point of view of lattice-parameter determination are as follows:

(a) a large number of reflections can be measured without realigning or removing the crystal;

(b) all the lattice parameters can be determined and not only one, as in the Bond (1960) method;

(c) the narrow diffraction profiles can be located with very high accuracy and precision;

(d) the arrangement makes it possible to remove some systematic errors;

(e) the high accuracy resulting from (a)–(d), which is comparable with that obtained by means of the Bond (1960) method;

(f) the high precision that results from (a) and (c).

A disadvantage, on the other hand, is the complicated interpretation (indexing) of multiple-diffraction patterns, so that this method is less popular than the Bond (1960) method.

The Post (1975) method has been applied to the accurate lattice-parameter determination of germanium, silicon, and diamond single crystals (Hom, Kiszénick & Post, 1975).

### 5.3.3.7. Multiple-crystal – pseudo-non-dispersive techniques

#### 5.3.3.7.1. Double-crystal spectrometers

Detailed information concerning the double-crystal spectrometer, which consists of two crystals successively diffracting the X-rays, can be found in James (1967, pp. 306–318), Compton & Allison (1935), and Azároff (1974). This device, usually used for wavelength determination, may also be applied to lattice-parameter determination, if the wavelength is accurately known. The principle of the device is shown in Fig. 5.3.3.8. The first crystal, the monochromator, diffracts the primary beam in the direction defined by the Bragg law for a given set of planes, so that the resulting beam is narrow and parallel. It can thus be considered to be both a collimator (or an additional collimator, if the primary beam has already been collimated) and a wavelength filter. The final profile  $h(\theta)$ , obtained as a result of the second diffraction by the specimen when the first crystal remains stationary and the second is rotated, is narrower than that which would be obtained with only one crystal. The final crystal profile  $h_c(\theta)$  [cf. equation (5.3.1.6)] is due to both crystals, which, if it is assumed that they are cut from the same block, can be described by the autocorrelation function (Hart, 1981):

$$h_c(\theta) = K \int_{-\infty}^{\infty} R(\theta') R(\theta' - \theta) d\theta', \quad (5.3.3.37)$$

where  $R(\theta)$  is an individual reflectivity function of one crystal and  $K$  is a coefficient of proportionality. Its half-width is 1.4 times larger than that related to only one crystal. In spite of this, the recorded profile can be as narrow as, for example,  $2.6''$  (Godwod, Kowalczyk & Szmid, 1974), since the profile due to the wavelength  $h_i(\theta)$ , modified by the first crystal, is extremely narrow. Additional advantages of the diffraction profile are: its symmetry, because  $h_c(\theta)$  is symmetric as an effect of autocorrelation, and smoothness, as an effect of additional integration. The profile can thus be located with very high accuracy and precision.

When there is a small difference in the two lattice spacings, so that one has a value  $d$  and the other  $d + \delta d$ , if  $\delta \lambda/\lambda$  is small enough, it can be assumed that the profile does not alter in shape but in its peak position [cf. §5.3.3.4.3.3, paragraph (3)]. If for two identical crystals this were located at  $\theta_0$ , the peak position

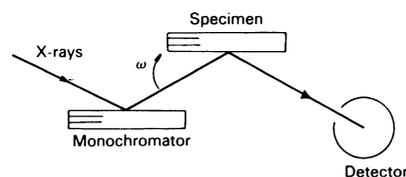


Fig. 5.3.3.8. Schematic representation of the double-crystal spectrometer.