knowledge concerning the given measurement, necessary for planning and performing the experiment and for estimating parameters being determined. The use of an incorrect model results in a bias, *i.e.* an additional systematic error that may appear aside from physical and geometric aberrations. Therefore, the choice of a well founded model is essential in accurate measurements.

In the case of lattice-parameter determination, the object of direct measurements is a diffraction profile, already mentioned in Subsection 5.3.1.1, and the quantity that is directly determined from the experiment is the Bragg angle θ.

The *a priori* information about the diffraction profile should define: (i) the way in which the Bragg angle θ is related to the measured profile $h(\omega)$, *i.e.* a measure of location; (ii) the mean values of the measured intensities within the profile; and (iii) their variances.

(i) In traditional photographic methods, the Bragg angle is determined from the measurement of distance on the film, where points or lines of the most intense blackening are taken into account. The blackening, which corresponds to the recorded intensity, may be estimated qualitatively ('by eye') or quantitatively, by means of a special device. In the second case, the intensity is determined as a function of the coordinates on the photograph, which, in turn, are related to the angular positions of diffracted beams. The distribution so obtained, *i.e.* the line profile or the diffraction profile, allows more precise measurements of the distances and the determination of θ angles, if a definition of the point (θ_0, h_0) of the profile $h(\theta)$, corresponding to the Bragg angle, *i.e. a measure of location*, is accepted. The analogous situation appears when the diffraction profile is recorded by means of the counter diffractometer. Then the intensities are measured by a counter, while the angular positions of the detector (2θ scan) or the sample (θ scan), or both (ω–2θ scan), are controlled by stepping motor. The device is normally combined with a computer, which facilitates the data processing.

There are various measures of location of the diffraction profile (Wilson, 1965; Thomsen & Yap, 1968). The most popular are:

(1) the centroid or the centre of gravity, defined as

$$\theta_c = \int_{\Omega_1}^{\Omega_2} \theta h(\theta)\,\mathrm{d}\theta \Big/ \int_{\Omega_1}^{\Omega_2} h(\theta)\,\mathrm{d}\theta, \qquad (5.3.3.6)$$

where Ω_1 and Ω_2 are the selected truncation limits;

(2) the median, the value θ_m that equally divides some specified portion of the line profile, *i.e.*

$$\int_{\Omega_1}^{\theta_m} h(\theta)\,\mathrm{d}\theta = \int_{\theta_m}^{\Omega_2} h(\theta)\,\mathrm{d}\theta; \qquad (5.3.3.7)$$

(3) the geometrical peak – the abscissa value θ_p for which the maximum occurs, *i.e.*

$$[\mathrm{d}h(\theta)/\mathrm{d}\theta]_{\theta=\theta_p} = 0; \qquad (5.3.3.8)$$

(4) the extrapolated peak or the midchord peak, introduced by Bearden (1933) – the point $\theta_{\rm ep}$ of intersection of two curves, one of them approximating the midpoints of chords drawn through the profile parallel to the abscissa axis (or to the background) and the other approximating the data points (Fig. 5.3.3.2);

(5) the single midpoint of a chord $\theta_{\rm mc}$ drawn horizontally at the defined height, αH, where H is the peak height and α is the truncation level, $0 < \alpha < 1$.

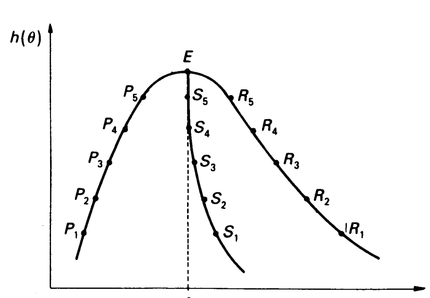

Fig. 5.3.3.2. The extrapolated-peak procedure (after Bearden, 1933).

The advantages and disadvantages of these measures of location have been widely discussed (Wilson, 1965, 1967; Thomsen & Yap, 1968; Segmüller, 1970; Kirk & Caulfield, 1977; Grosswig, Jäckel & Kittner, 1986; Gałdecka, 1994), the errors, both systematic (biases) and statistical (variances), resulting from each of these definitions being taken into account. The dependence of these errors on the scanning range (truncation limits) is of great importance. Such features of the definitions as their simplicity or current usage were also considered.

The geometrical peak of the least-squares parabola, approximating the data points near the top of the profile, distinguishes itself with the best precision but rather large bias (because of the asymmetry of the profiles met in practice); the extrapolated peak – commonly used in the case of the Bond (1960) method (definition 4) – permits location of the peak with better accuracy and omitting the dispersion error (*cf.* §5.3.3.4.3.2). The centre of gravity, very useful in theoretical considerations (Wilson, 1963), is strongly dependent on the truncation limits and requires a rather large scanning range. The choice of the definition of the measure of location is the first step of lattice-parameter calculations and also of systematic and statistical error estimation.

In the papers that appeared in the mid-1950's, and which were mainly concerned with powder samples, the centre of gravity as a measure of location was more often used than the peak, probably owing to its property of additivity (the total systematic error in the Bragg angle is a sum of the partial errors related to various physical and apparatus factors) and the estimated errors were consequently referred to this point. The papers were reviewed by Wilson (1963, 1980), one of the authors, in the form of a homogeneous mathematical theory of X-ray powder diffractometry. Some of the formulae describing corrections for displacements of the centroid caused by physical and geometrical factors (collected in convenient tables) proved to be useful for single-crystal methods as well (Smakula & Kalnajs, 1955; Kheiker & Zevin, 1963). Wilson (1963) derived the general formula for calculations of the peak displacements due to various factors. As results from this, the displacements are not additive and, in the case when at least one of the partial distributions is asymmetric, the convolution of the curves [see equation (5.3.1.6)] may lead to an appreciable peak shift, if the distributions are not known. The problem has been treated by Berger (1984, 1986*a*), who used computer modelling.

In later single-crystal methods, in particular in the Bond (1960) method, the peak position of the profile was determined rather than the centroid and the respective corrections referred to the peak (§5.3.3.4.3.2). As a rule, the corrections that related to the peak position were treated as being independent. In practice, this simplifying assumption can be sufficient in measurements with moderate and even high accuracy. However, if the highest accuracy, say of 1 part in 10^7, is required, the joint effect of all the aberrations should be considered (the so-called 'cross terms' are used besides the main terms). Such considerations [Härtwig & Grosswig, 1989; *cf.* §5.3.3.4.3.2, point (7)] must be based on a well-founded physical model of the diffraction profile.