since standard X-ray tubes readily produce divergent beams, the next evolutionary step was to employ self-focusing geometries, as first proposed independently by Seemann (1919) and Bohlin (1920), termed 'Seemann–Bohlin geometry'. In addition to significantly improved resolution, the intensity was also greatly increased by using a para-focusing arrangement using an X-ray source and specimen with finite width (line focus). Guinier (1937) extended the Seemann–Bohlin geometry using an incident-beam monochromator. Although the monochromator significantly reduced the intensity, this disadvantage was overcompensated for by improved beam conditioning, leading to unparalleled resolution at that time and elimination of the $K\alpha_2$ component of the radiation. This made the Guinier camera the best-performing film camera at that time and it therefore enjoyed high popularity.

The idea of using powder diffraction for phase identification of substances in pure form or in mixtures, originally suggested by Hull (1919) and then formalized by Hanawalt *et al.* (1938), attracted enormous interest, and developed into the powder diffraction method, making it a fundamental tool for material scientists. However, while classic film cameras laid down the historical foundation for the success of polycrystalline diffraction, their use was mostly limited to phase identification, semi-quantitative phase analysis and macroscopic stress measurements. Inherent difficulties included, but were not limited to, obtaining reliable intensities (because of film grain size and nonlinearity of the film response), very limited flexibility in terms of hardware extensions such as non-ambient specimen stages, and lack of diffracted-beam conditioning (*e.g.* the use of diffracted-beam monochromators).

Detailed descriptions of the many camera types as well as their use are given in a large number of texts. The interested reader is specifically referred to the textbook of Klug & Alexander (1974), which also contains an extensive bibliography.

2.1.3.1.2. *Diffractometers*

Photographic films have two important weaknesses: the detection efficiency is low and quantification of the diffracted intensities, including the line-profile shapes, is indirect and cumbersome. These shortcomings led to the idea of replacing the film with a photon counter (most commonly utilizing the Geiger–Müller counter at that time) and thus to the development of a device called a 'diffractometer'. The design resembled that of the Bragg ionization spectrometer, but dispersed monochromatic radiation from lattice planes rather than a spectrum of X-ray wavelengths. The first diffractometer developed by Le Galley (1935) was a non-focusing arrangement using a point-focus X-ray tube, making use of the cylindrical geometry of a normal film camera. In subsequent instrument designs focusing geometries were adopted, mostly the 'Bragg–Brentano geometry' (Brentano, 1924), a modification of the Seemann–Bohlin geometry, first introduced by Lindemann & Trost (1940) and Friedmann (1945).

The introduction of the first commercial focusing diffractometer in the early 1950s resulted in another major advance of the polycrystalline diffraction method, and may be largely credited to Parrish and co-workers (*e.g.* Parrish, 1949). This instrument consisted of a fixed-anode X-ray tube and a mechanical goniometer, operating in Bragg–Brentano geometry. The initial replacement of photographic film by the Geiger–Müller counter, and soon after by scintillation and lithium-drifted silicon detectors, allowed accurate intensities and line-profile shapes with high resolution to be recorded. The large space around the specimen permitted the design of various interchangeable stages for specimen rotation and translation, automatic specimen changing and non-ambient analyses. As a consequence, powder diffraction found many new applications beyond phase identification, including, but not limited to, quantitative analysis of crystalline and amorphous phases, microstructure analysis, and texture and strain analysis, at ambient and non-ambient conditions.

In the following decades, diffractometers were fully automated, fully digitized, and electronically and mechanically stabilized. The data quality they delivered became generally superior to that of film cameras, including in terms of resolution, eventually even facilitating structure determination and refinement from powders. Attempts to improve Guinier or Seemann–Bohlin cameras by replacing the film with image plates or any other stationary or scanning detectors did not produce competitive instrumentation in terms of instrument flexibility and mechanical simplicity. As a result, film cameras were steadily replaced by automated diffractometers using the Bragg–Brentano geometry. Since the 1990s, classic film cameras as well as other Guinier- or Seemann–Bohlin-based instruments are no longer used in practical polycrystalline diffraction analysis and thus lost any commercial relevance, apart from for a few niche applications. The Bragg–Brentano geometry, as developed in the 1940s, became the dominating instrument geometry and accounted for more than 90% of all instruments sold. The remainder almost exclusively used Debye–Scherrer-type arrangements, either employing focusing incident-beam monochromators for flat-plate or capillary transmission setups, or parallel-beam setups based on (pinhole) slits and/or Soller collimators and/or channel-cut monochromators for micro-diffraction, small-angle X-ray scattering and the characterization of thin films.

While powder diffractometers have changed little in their construction and geometry since the 1940s, considerable advances have made in X-ray detection and X-ray beam conditioning (X-ray optics).

Significant detector developments include one- and two-dimensional position-sensitive detectors (PSDs) based on gas proportional counter technology, and especially that of the scanning one-dimensional PSD (Göbel, 1980). The replacement of a point detector by a scanning one-dimensional PSD allowed the measurement time required to record a full pattern to be reduced down to minutes without significant compromise on resolution. This enabled time-critical applications (such as non-ambient and high-throughput analyses), or compensation of the intensity loss when employing incident-beam monochromators.

The introduction of laterally graded multilayers on figured reflectors, so-called 'Göbel mirrors' (Schuster & Göbel, 1996), allowed the conversion of a convergent beam into a parallel beam, and thus added a new dimension to laboratory beam conditioning – at a time when X-ray techniques were expanding into the now very rapidly growing area of thin-film characterization, sparking a renaissance of the Debye–Scherrer geometry.

Until the late 1980s and early 1990s, traditional powder diffraction and thin-film characterization were seen as two different techniques with diverse requirements. As a consequence, thin-film techniques formed a different X-ray diffraction application sector, served by different and specialized instrumentation, in addition to the already existing distinction between single-crystal and powder diffraction applications and instrumentation. The X-ray powder diffraction market was characterized by dedicated (and separately marketed) instruments for traditional powder diffraction, usually based on the Bragg–

Brentano geometry, and for thin-film analysis, usually based on the Debye–Scherrer geometry.

2.1.3.2. *Recent years*

In the 1990s, more and more laboratories started to deal with a full range of materials and related applications - from powders through polycrystalline thin films to epitaxial thin films. Dedicated and inflexible instruments were no longer economic for serving the increasing range of applications and also their increasing data-quality requirements.

The growing need for multipurpose instrumentation led to a new generation of X-ray diffractometers in the late 1990s, from all of the major manufacturers, based on a platform concept covering all relevant beam-path components including X-ray sources, optics, specimen stages and detectors. This concept, described in Section 2.1.4, allowed for a faster development of more and more differentiated instrumentation to optimally meet the requirements of all possible applications and sample types. Particularly successful were design improvements that allow the user to transform an instrument on-site by changing beam-path components, often without any need for alignment or even tools, to cover a larger range of applications and sample types using a single instrument.

A major contribution to the platform concept came from the continued development of beam conditioners based on multilayers, resulting in a wealth of X-ray beam optics for different applications. Advanced sputtering techniques allow the fabrication of multilayer optics with virtually arbitrary beam divergence, which can be used to generate focusing, parallel and divergent beams for both point- and line-focus applications.

The introduction of a series of new detector technologies in the early 2000s represented another technological quantum leap, which completely changed the X-ray detection landscape for laboratory diffraction. Within only a few years, detectors based on silicon micro-strip, silicon pixel and micro-gap technologies reached a market share of more than 90% in newly sold systems. Proportional and scintillation point detectors will probably become obsolete in only a few years from now, but can still be found, usually in lower-budget systems.

Today's instruments, with their different possible configurations of beam-path components, are now capable of performing a wider range of X-ray scattering applications than ever (see Section 2.1.4.3). Not surprisingly, the platform concept has become so successful that all modern X-ray diffractometers are now, at least to some extent, equipped with interchange capabilities for beam-path components. However, the fundamental principles remain the same and date back to the first film cameras and diffractometers, no matter how advanced today's instrumentation is.

2.1.4. The platform concept – fitting the instrument to the need

Modern X-ray diffractometers are highly modular assembly systems based on a platform concept, with a shared set of major components over a number of distinct diffractometer models, serving different X-ray scattering application areas. Such a platform concept has two important advantages. Firstly, a common design allows differentiated instruments to be developed faster, and eases the integration of new or improved beam-path components, potentially over the whole model range. Secondly, it enables the design of an X-ray optical bench with on-site interchange capabilities, allowing the mounting of selected beam-path components to meet specific application and specimen-property requirements.

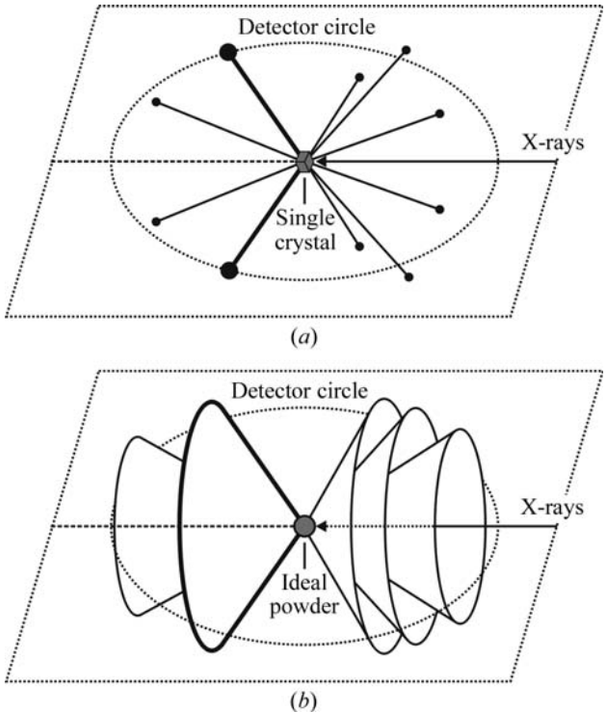

Figure 2.1.1
Diffraction of X-rays by (*a*) a rotating single crystal and (*b*) an ideal powder. The scattered intensity may be measured by a detector placed on the detector circle.

2.1.4.1. *Basic design principles and instrument geometry considerations*

X-ray scattering data are generally recorded in what is virtually the simplest possible manner, where the scattered intensity is measured by a detector mounted at some distance from the specimen. This is illustrated in Fig. 2.1.1, where a narrow, essentially monochromatic beam illuminates a small spherical specimen. For a rotating single crystal, the diffracted beams point in discrete directions in space as given by Bragg's law for each lattice vector d_{hkl} (Fig. 2.1.1*a*). For an ideal powder consisting of a virtually unlimited number of randomly oriented crystallites, the diffracted beams will form concentric cones ('Debye cones') with a semi-apex angle of 2θ, representing all randomly oriented identical lattice vectors d_{hkl} (Fig. 2.1.1*b*). Note that in contrast to a single crystal, an ideal powder does not need to be rotated to obtain a complete powder diffraction pattern.

Most instruments are built around a central specimen and consist of the following beam-path components, the numbering of which is consistent with the mounting positions shown in Fig. 2.1.2:

(1) X-ray source;
(2) incident-beam optics;
(3) goniometer base or specimen stage;
(4) diffracted-beam optics;
(5) detector.

The directions of the *incident* and *diffracted beams* (also called 'primary' and 'secondary' beams) form the *diffraction plane* (also called the 'equatorial plane' or 'scattering plane'). The goniometer base can be mounted horizontally (horizontal diffraction plane) or vertically (vertical diffraction plane). The direction perpendicular to the equatorial plane is known as the *axial*