2. INSTRUMENTATION AND SAMPLE PREPARATION

Table 2.1.2
X-ray applications for with modern X-ray diffractometers

X-ray scattering
Powder diffraction
Qualitative (phase identification) and quantitative phase
analysis
Indexing, structure determination and structure refinement
from powder data
Microstructure analysis (texture, size, strain, microstrain,
disorder and other defects)
Pair distribution function analysis ('total scattering')
Thin-film analysis
Grazing incidence X-ray diffraction (GIXRD)
X-ray reflectometry
Stress and texture
High-resolution X-ray diffraction
Reciprocal-space mapping
In-plane GIXRD
Single-crystal diffraction
Chemical crystallography
Protein crystallography
Small-angle X-ray scattering
X-ray topography
X-ray absorption
X-ray radiography (X-ray-absorption-based imaging)
X-ray emission
X-ray fluorescence

specimen. X-rays that pass through the specimen can be detected to give a two-dimensional representation of the absorption contrast within the specimen. For tomography, the X-ray source and detector will be moved to blur out structures not in the focal plane. Multiple images can be used to generate a three-dimensional representation of the specimen by means of computed tomography. Obvious disadvantages are the large effective focal spot size of the X-ray sources and the relatively low resolution of the detectors that are typically used for powder diffraction, which, in combination with a limited adjustability of both the X-ray-source-to-specimen and specimen-to-detector distances, lead to substantial unsharpness issues and poor resolution. High-quality images can be achieved when using micro-focus X-ray sources and charge-coupled device (CCD) detectors with focus and pixel sizes smaller than 10 µm, respectively, but such an instrument configuration is not suitable for applications requiring ideal powders (see also Sections 2.1.6 and 2.1.7).

Collecting X-ray fluorescence data is comparatively straightforward. Data can be collected simultaneously to X-ray scattering data when employing a suitable detector, such as an energy-dispersive detector (Section 2.1.7.2.3). There are a couple of disadvantages to be considered, such as absorption issues (the specimen will be normally measured in air rather than in vacuum, hampering the analysis of light elements) and the inefficiency of excitation by the characteristic line energies of the X-ray source anode materials typically used for diffraction (hampering the analysis of elements with higher atomic numbers than that of the anode material).

2.1.5. Goniometer designs

A goniometer, by definition, is an instrument that either measures an angle or allows an object to be rotated to a precise angular position. In an X-ray diffractometer the purpose of the goniometer is to move the X-ray source, specimen and detector in relation to each other. Goniometers are usually categorized by the number of axes available for X-ray source, specimen and

detector rotation, and are thus called one-, two-, three-, . . . , n-axis (or -circle) goniometers.

Because of practical reasons, most goniometers consist of two distinct components, a goniometer base and a specimen stage, with the specimen stage mounted on the goniometer base.

The goniometer base typically offers two axes, one axis to rotate the X-ray source or the specimen stage, the other axis to rotate the detector. In some designs goniometer bases are omitted, specifically if there is no need to move the X-ray source and the detector, such as in Debye–Scherrer-type diffractometers with large detectors. Such machines are usually dedicated to a particular application without the need for high flexibility.

Depending on the requirements of the application, additional rotational and translational degrees of freedom may be needed to rotate and translate a specimen in space; these are usually implemented in the specimen stage. More rotational degrees of freedom may include the rotation of the X-ray source line focus or a rotation of the detector out of the diffraction plane to measure diffraction by lattice planes (nearly) perpendicular to the specimen surface, so-called non-coplanar diffraction.

2.1.5.1. *Geometrical conventions and scan modes*

In the literature there is some inconsistency related to the naming of axes and the choice of signs for angles (left- *versus* right-handed). A comprehensive treatment of geometrical conventions has recently been given by He (2009); in the following these conventions will be adhered to.

In many texts the notations θ–2θ and θ–θ rather than ω–2θ and ω–θ are used, mostly because of historical reasons. The first diffractometers operated in Bragg–Brentano geometry (see Section 2.1.3.1.2) and were equipped with single-axis goniometers. In such a goniometer the single axis drives two shafts which are mechanically coupled 1:2 or 1:1; thus the notations θ–2θ and θ–θ were coined. Today, the majority of all goniometer bases allow coupled as well as uncoupled rotation of the ω and θ axes. Therefore the ω–2θ and ω–θ notations should be generally preferred, as they represent the more general notations.

2.1.5.1.1. *Goniometer base*

A typical goniometer base provides two coaxial and independently driven axes, ω and 2θ, mounted perpendicular to the diffraction plane. These two axes are the main axes of a goniometer, since they have the most effect on the accuracy and precision of measured Bragg angles. The diffraction plane and the axes are generally described by a right-handed Cartesian coordinate system, as illustrated in Fig. 2.1.6, where the direct X-ray beam propagates along the X_L axis. Z_L is up and coincident with the ω and 2θ axes, and X_L–Y_L define the diffraction plane with the detector circle coplanar to it. Since X_L is coincident with the incident X-ray beam, it is also the axis of the Debye cones. The semi-apex angles of the cones are determined by the 2θ values given by the Bragg equation. The angles 2θ and γ describe the direction of scattering vectors in space (compare Fig. 2.1.1), where γ is defined as the azimuthal angle from the origin at $-Z_L$ with a right-hand rotation axis along the opposite direction of the incident beam ($-X_L$ direction).

The ω and 2θ axes are mechanically arranged as the inner circle and outer circle, respectively. The inner circle usually carries either the specimen stage or the X-ray source, while the detector is mounted on the outer circle. As a consequence, there are two common base goniometer configurations in use: In the ω–2θ (or θ–2θ with $\omega = \theta$) configuration, the incident-beam direction is
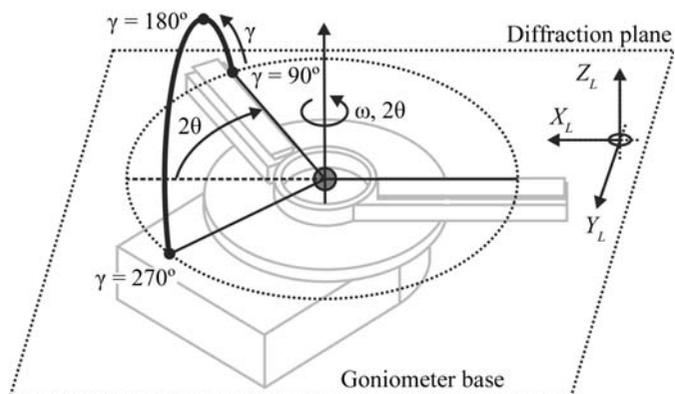
Figure 2.1.6
Laboratory coordinates and geometric definition of the coaxial goniometer axes ω and 2θ. If the azimuthal angle γ takes all values from 0 to 360° at a given Bragg angle 2θ, the trace of the diffracted beams forms a Debye cone (compare with Fig. 2.1.1).

mechanically fixed. The ω axis rotates the specimen stage, while the 2θ axis rotates the detector. In the ω–θ (or θ–θ with $\omega = \theta$) configuration, the ω axis defines the incident-beam angle by rotating the X-ray source, while the other axis scans the detector. In this configuration the specimen stage is mechanically fixed. Both configurations allow identical positioning of the X-ray source, specimen and detector relative to each other.

The goniometer base orientation is defined by the diffraction plane, which can be either horizontal or vertical. Vertical-base goniometers in ω–θ configuration are particularly popular, as the specimen is always kept horizontal, effectively preventing it from falling off. However, heavy specimens and beam-path components require particular attention in both the goniometer base design and choice of orientation, as they have a strong impact on goniometer accuracy, precision and early wear and tear (see also Section 2.1.5.2). Where loads exceed the maximum specifications for a vertically mounted goniometer base, and whenever horizontal specimen positioning is not imperative, either a vertical goniometer base in ω–2θ configuration or a horizontal goniometer should be chosen.
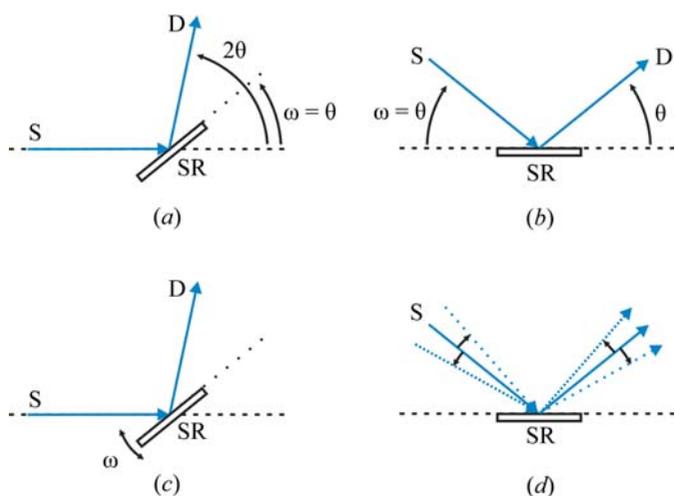

Figure 2.1.7
Goniometer base configurations and scan modes suitable for both Bragg–Brentano or Debye–Scherrer geometry. Symmetric beam path setup in (a) ω–2θ and (b) ω–θ configuration. Rocking curve setup in (c) ω–2θ and (d) ω–θ configuration. Only the central beams are shown for clarity, rotations are indicated by arrows. S: X-ray source, D: detector, SR: flat specimen, reflection mode.
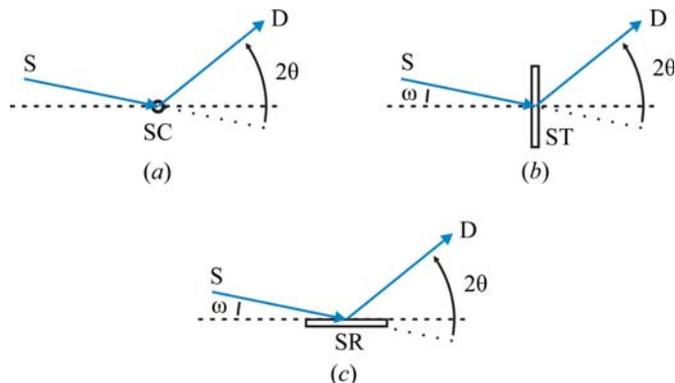

Figure 2.1.8
Goniometer base configurations and scan modes suitable for the Debye–Scherrer geometry only. Only the central beams are shown for clarity. (a) Capillary specimen in transmission mode, (b) flat specimen in transmission mode, (c) flat specimen in reflection mode, grazing incidence with fixed ω. S: X-ray source, D: detector, SR: flat specimen, reflection mode; SC: capillary specimen, transmission mode; ST: flat specimen, transmission mode.

In Figs. 2.1.7 and 2.1.8 a range of typical goniometer base configurations and scan modes are illustrated.

A symmetric beam-path setup in reflection mode, where both the incident and diffracted beam form an angle of θ with respect to the specimen surface, is mandatory for instruments operating in Bragg–Brentano geometry to maintain the focusing condition (see Section 2.1.4.1), but is also commonly used in Debye–Scherrer geometry. Scanning involves coupling of the ω (with $\omega = \theta$) and 2θ axes in a ratio of 1:2 for the ω–2θ configuration (Fig. 2.1.7a) and 1:1 for the ω–θ configuration (Fig. 2.1.7b), but only allows probing of lattice planes essentially parallel to the specimen surface. Where determination of a texture parameter is sought, a so-called 'rocking-curve' measurement can be performed by rocking either the specimen or the X-ray source and detector around the position of a Bragg peak. Two scenarios need to be considered and are illustrated in Fig. 2.1.7(c) and Fig. 2.1.7(d). In the ω–2θ configuration with fixed X-ray source (Fig. 2.1.7c), the detector will be fixed at the 2θ position of a selected Bragg peak, while the specimen is rotated ('rocked') independently, to perform a so-called 'ω-scan'. To achieve the same in an ω–θ configuration with fixed specimen, the X-ray source and the detector will be coupled 1:−1 or −1:1 to perform a clockwise or anticlockwise scan while maintaining the selected 2θ position, respectively, as illustrated in Fig. 2.1.7(d).

In Debye–Scherrer geometry there is no geometrical restraint requiring coupled scans to maintain 2θ-dependent focusing conditions, as is the case in the Bragg–Brentano geometry, providing high flexibility. Specimens can be measured in both reflection as well as transmission mode. In principle, the incident-beam direction may be any relative to the specimen surface, and can be fixed or variable, while the detector performs a 'detector scan'. The ω and 2θ axes may be coupled or not. Choices solely depend on the specimen properties and the requirements of the application. This is demonstrated in Fig. 2.1.8 for a few representative examples. The classic Debye–Scherrer geometry using a capillary specimen is shown in Fig. 2.1.8(a). The capillary specimen can be readily exchanged for a flat-plate specimen as shown in Fig. 2.1.8(b) and Fig. 2.1.8(c) for flat-plate transmission and reflection, respectively. ω can be set to different angles or perform a coupled scan to allow access to higher 2θ angles (Fig. 2.1.8b) or can be set to a different angle for grazing-incidence measurements (Fig. 2.1.8c). In some applications it may be beneficial to perform a (usually coupled) scan of both ω and 2θ to
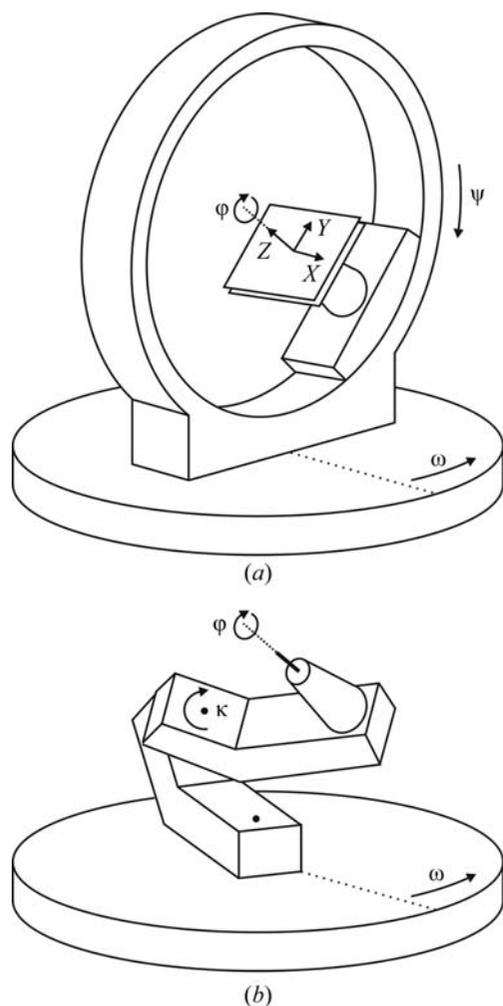
Figure 2.1.9
Geometric definition of the Eulerian and kappa geometries with identical specimen orientation in space. (*a*) Specimen rotation and translation in a Eulerian cradle equipped with an *XYZ* stage, (*b*) specimen rotation on a kappa stage.

improve particle statistics ('wobbling'). Obviously, all the setups shown in Fig. 2.1.8 will work for the full range of X-ray scattering and absorption techniques as discussed in Section 2.1.4.3, leading to the renaissance of the Debye–Scherrer geometry within the past 20 years.

2.1.5.1.2. *Specimen stage*

Depending on the requirements of the application, the specimen stage may offer additional degrees of freedom for specimen rotation as well as *X*, *Y*, *Z* translation. The goniometer base may be configured as ω–2θ as well as ω–θ, and may be oriented vertically as well as horizontally.

To orient a specimen in all possible orientations in space, the specimen stage will offer two more rotational degrees of freedom in addition to the ω and 2θ axes provided by the goniometer base. Such goniometers are known as four-axis diffractometers, with two basic geometries in common use for specimen orientation: Eulerian geometry and kappa geometry.

In the Eulerian geometry the specimen is oriented through the three Euler angles ω (defined by the ω axis of the goniometer base), ψ (psi), and φ (phi). The relationship between the laboratory and rotation axes is shown in Fig. 2.1.9(*a*) for a typical Eulerian cradle. The ω angle is defined as a right-handed rotation about the ω (or Z_L) axis. The ψ angle is a right-hand rotation about the ψ axis, which lies in the diffraction plane and runs

parallel to the bisectrix between the incident and diffracted beams. The φ angle defines a left-handed rotation about an axis on the specimen, typically the normal to a flat specimen surface. In some texts the angle χ (chi) is used instead of ψ, with the relationship between the two angles defined as $\psi = 90 - \chi$. Eulerian cradles have the advantage of high mechanical stability and are often integrated with *XYZ* stages to handle bulky specimens. The geometrical definitions of specimen *X*, *Y*, *Z* translations are also shown in Fig. 2.1.9(*a*).

The kappa (κ) geometry shown in Fig. 2.1.9(*b*) represents an alternative way to orient a specimen in space. The ψ axis of the Eulerian geometry is replaced by the κ axis, which is tilted at 50° relative to the diffraction plane. It supports an arm carrying the specimen, with the φ axis tilted at 50° to κ. The role of the Eulerian ψ rotation is fulfilled by means of combined rotation along κ and φ, which allows Eulerian ψ angles in the range -100 to $+100°$ to be obtained. The absence of the (bulky) ψ circle of Eulerian cradles allows an unobstructed view of the specimen and unhindered access from 'above', for example to mount a cooling device without risk of collision. These two advantages made the kappa geometry popular in single-crystal work. On the other hand, it is not possible to move the specimen to an 'upside-down' position, *i.e.* equivalent to Eulerian ψ angles less than $-100°$ or greater than 100°.

Most goniometers do not offer all six rotational and translational degrees of freedom. The majority of these are actually three-axis goniometers, where the specimen stage offers one additional axis for specimen rotation.

A comprehensive overview of commercially available specimen stages is beyond the scope of this chapter owing to the huge number of dedicated specimen stages available for different kinds of specimen types, levels of automation and non-ambient analyses. The most complete and most current information will be found in manufacturers' product information.

2.1.5.2. *Accuracy and precision*

Particularly high demands are made on goniometer accuracy and precision in Bragg-angle positioning (goniometer base) and specimen orientation (specimen stage). These are usually expressed by the angular accuracy and precision of the goniometer-base axes (ω, 2θ) and the sphere of confusion of specimen positioning in space. A detailed discussion is given by He (2009).

Depending on the application and the actual instrument configuration, additional requirements may be imposed on goniometers, and may limit the maximum accuracy and precision that are achievable. Typical requirements, often not compatible with each other, are:
(*a*) mounting of heavy and bulky beam-path components and specimens;
(*b*) variable goniometer radii, typically ranging from about 15 to 60 cm; and
(*c*) vertical goniometer operation to prevent specimens from falling off the holder.

Each of these requirements may have an impact on goniometer accuracy and precision, and potential early wear and tear. Typical loads range from several kg for fixed-target X-ray sources up to 50 kg and more for moving-target X-ray sources. Small detectors such as point and one-dimensional detectors range from less than 1 kg up to a few kg, while large two-dimensional detectors may weigh up to 50 kg and sometimes even more.

For vertical goniometers, the loads on the main axis bearings can be effectively reduced by counterbalances, as shown in Fig.
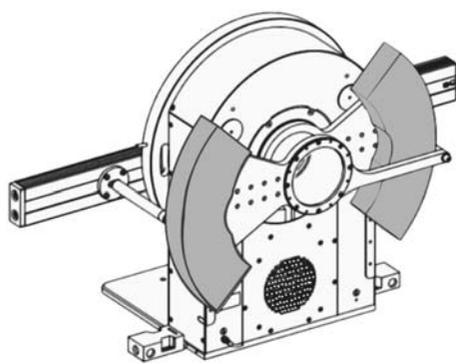
Figure 2.1.10
Example of counterbalancing of a vertical θ–θ goniometer. The counterweights (grey parts) are located at positions matching the weights and locations of the X-ray source and detector. Mounting of different beam-path components with significantly different weight or moving of, for example, the X-ray source and/or the detector to change the respective radii may require repositioning of the counterweights to maintain goniometer accuracy and instrument alignment.

2.1.10 for a goniometer in the ω–θ configuration. Heavy specimen stages may also be supported from below or mounted directly on the bench, disconnected from the goniometer base. However, for heavy beam-path components and larger goniometer radii there is the additional issue of high torques on the incident- and/or the diffracted-beam X-ray optical benches, leading to torsions along the benches. These may significantly deteriorate both the angular accuracy of a goniometer and instrument alignment. For heavy incident-beam-path components such as moving-target X-ray sources, a vertical goniometer base in the ω–2θ configuration is commonly used, as the incident-beam optical X-ray bench is mechanically fixed. For heavy incident- and diffracted-beam-path components a horizontal goniometer base is preferred.

Modern goniometers are equipped with stepping motors and optical encoders, and feature life-span lubrication for maintenance-free operation. The typical accuracy of the two goniometer base axes (ω, 2θ) is of the order of a few thousandths of a degree, with a precision of the order of a few tens of thousandths of a degree. The ψ and φ axes of the specimen stage are mostly used for specimen orientation; the typical angular accuracy and precision are in the range of about 0.01°.

The sphere of confusion of a goniometer is the result of a superposition of all axes and represents the minimum spherical volume covering all possible locations of an infinitely small specimen at all possible orientations. The size of the sphere of confusion depends on issues such as individual axis accuracy and precision, mechanical tolerances, thermal-expansion mismatches, and the weights of the specimen and beam-path components. The sphere of confusion for a two-axis goniometer or a four-axis goniometer with a kappa stage is typically less than 10 µm, and for a four-axis goniometer with a Eulerian cradle less than 50 µm; both values are without a specimen loaded.

Note that the final accuracy of the Bragg angles of the measurement data is mostly determined by instrument alignment, and not by the accuracy specifically of the two goniometer base axes. Optical encoders can measure and control axis positions, but they cannot detect any misaligned or even loose beam-path components. The final data accuracy is determined by the adjustability of an X-ray diffractometer with all its beam-path components. A modern X-ray diffractometer can be aligned to an angular accuracy of equal or better than 0.01° 2θ, which can be checked using suitable standard reference materials (see Chapter 3.1).

2.1.5.3. *Hybrid beam-path systems*

The trend towards multipurpose instrumentation as well as specific application requirements has led to a few specialized goniometer designs. Two major representatives of such designs are (1) multiple-beam-path systems and (2) systems with additional rotational degrees of freedom of beam-path components, such as is required for non-coplanar grazing-incidence diffraction (GID).

2.1.5.3.1. *Multiple-beam-path systems*

Multiple-beam-path systems are usually characterized by integrating more than one beam path on a single goniometer, employing different, complementary beam-path components to meet different application and specimen-property requirements. Mounting two different fixed-target X-ray sources (usually microsources) with different wavelengths (Cu, Mo) is very popular in single-crystal crystallography. Double detector arms are used to mount different types of detectors, most frequently one-dimensional detectors in combination with point detectors. Different X-ray optics can be used to implement different instrument geometries.

A significant driving force behind such multipurpose instrumentation is convenience, *i.e.* to serve a maximum range of applications and specimen types, ideally without the need to manually change the instrument configuration. Indeed, switching between different, preconfigured beam paths may often only require the push of a single software button. However, parallel mounting of different beam-path components raises issues related to the goniometer load and to limitations of angular scan ranges owing to collision issues.

In more recent designs, different X-ray optics have been combined into single motorized modules, allowing switching between different beam paths. Such 'combi-optics' are described in Section 2.1.6.3.4.

2.1.5.3.2. *Non-coplanar beam-path systems*

Non-coplanar (or 'in-plane') grazing-incidence diffraction is a technique for investigating the near-surface region of specimens (ten or fewer nanometres beneath the air–specimen interface). It exploits the high intensity of the total external reflection condition while simultaneously involving Bragg diffraction from planes that are nearly perpendicular to the specimen surface.

As illustrated in Fig. 2.1.11, the incident beam is set at an angle α_I, enabling total external reflection in the coplanar direction (that is coplanar to the diffraction plane); related applications include reflectometry and grazing-incidence small-angle X-ray scattering (GISAXS). 'In-plane' grazing-incidence diffraction
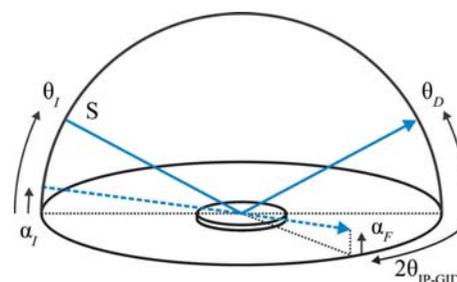

Figure 2.1.11
Illustration of coplanar and in-plane diffraction. S: X-ray source. θ_I, θ_D: incident and diffracted beams for coplanar diffraction. α_I, α_F, $2\theta_{IP\text{-}GID}$: incident-beam angle, exit angle and diffracted-beam angle, respectively, for in-plane grazing-incidence diffraction.
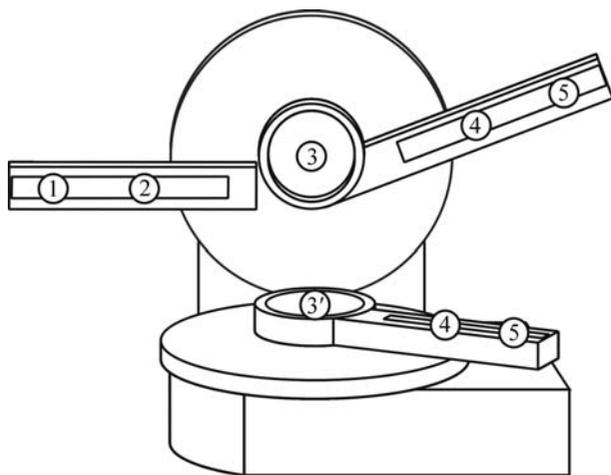
Figure 2.1.12
Sophisticated IP-GID implementation by placing two goniometers vertically with respect to each other, allowing simultaneous coplanar and in-plane measurements using two independent scattered-beam optical X-ray benches (compare with Fig. 2.1.2). The sample stage may be mounted at position 3 or 3′.

(IP-GID) may be measured at angles $2\theta_{\text{IP-GID}}$ in the non-coplanar direction at an exit angle α_F.

There are two principal instrument designs implementing coplanar and in-plane data collection. Firstly, as is obvious from Fig. 2.1.11, a dual-goniometer system may be employed. The most sophisticated implementation has two goniometers placed vertically one above the other, allowing simultaneous coplanar and in-plane measurements using two independent scattered-beam optical X-ray benches as shown in Fig. 2.1.12. Alternatively, the second goniometer may be integrated into the scattered-beam optical X-ray bench, allowing sequential coplanar and in-plane measurements. As a further alternative, a single goniometer may be used, with a Eulerian cradle mounted at the detector position, allowing the detector to be moved around the specimen to perform in-plane measurements. Secondly, a single goniometer equipped with a Eulerian cradle may be used, where the specimen is simply turned by 90° in ψ. As line focus is usually employed for IP-GID measurements, the X-ray source is also turned by 90° to increase the flux.

For all systems, the diffracted-beam optical X-ray benches may be equipped as for multiple beam-path systems, as described in Section 2.1.5.3.1, providing extremely high flexibility. The choice of the most appropriate design depends on issues such as specimen size and weight, the weight of any components in the diffracted-beam path, related spheres of confusion, and the potential need to measure the specimen in a horizontal position.

2.1.6. X-ray sources and optics

This section covers both the generation as well as the conditioning of X-ray beams. All types of X-ray sources, whether laboratory or synchrotron sources, emit a wide range of wavelengths with a characteristic beam divergence and with an intensity related to the power load applied. The function of the incident- and diffracted-beam X-ray optics is to condition the emitted beam in terms of desired wavelength spread, divergence, cross-section size, and shape, and to conserve as much intensity as possible. To achieve maximum performance in terms of intensity and angular resolution, it is essential to design the X-ray optics so that their properties match the characteristics of the X-ray source. Important parameters are the X-ray source beam size and shape, as well as the acceptance angle of the optics given by their design and the distance to the X-ray source.

The optimum choice of an X-ray source and the X-ray optics always depends on the properties of the specimen and the requirements of the applications. Applications requiring high spatial resolution (*e.g.* small single crystals or microdiffraction) or low-angle scattering (*e.g.* thin-film analysis or SAXS) usually require parallel and narrow beams, while diffraction by ideal powders usually works best with larger and slightly divergent beams. As X-ray sources are hardly ever used without X-ray optics, all the components should be seen as one unit determining the beam characteristics at the specimen and eventually at the detector position.

2.1.6.1. *X-ray beam quality measures*

An X-ray beam is characterized by its intensity, wavelength spread, divergence, cross-section size, homogeneity and shape. Simple means for quantifying the quality of an X-ray beam are often useful, and can be used to design an optimal measurement setup by appropriate choice of a combination of X-ray source and X-ray optics. The quantities that are typically used are flux, flux density, brightness and brilliance, all within a 0.1% bandwidth represented by a wavelength range, $\Delta\lambda$, centred around a specific wavelength λ, *i.e.* $\Delta\lambda$ is equal to 1/1000 of λ. While flux, flux density, brightness and brilliance are inter-related, they are distinct and one thus has to consider all of these when comparing X-ray beam characteristics.

Flux represents the integrated intensity of an X-ray beam and is defined as the number of X-ray photons emitted per unit time. The unit for flux is photons per second (p.p.s.).

Flux density is defined as the flux passing through a unit area. The unit is p.p.s. mm^{-2}. Flux density is an appropriate parameter for measuring local counting rates and is synonymous to the term 'intensity' as used in colloquial speech.

Brightness takes the beam divergence into account, and is defined as the flux per unit of solid angle of the radiation cone. The unit is p.p.s. mrad^{-2}. Brightness is an appropriate parameter to use when comparing two X-ray sources with identical focal spot size, as the definition does not contain a unit area.

Brilliance additionally takes the beam dimensions into account and is defined as brightness per mm^2. The unit is p.p.s. mm^{-2} mrad^{-2}. Brilliance is maximized by making the beam size and divergence as small as possible, and the photon flux as large as possible. Two X-ray beams may have the same flux density but different brilliance if the two beams have different beam divergence. Brilliance is thus an appropriate parameter to use when comparing two X-ray sources with different focal spot sizes.

Note that the X-ray source brilliance is an invariant quantity, *i.e.* the brilliance at the specimen position cannot be improved by any optical techniques, but only by increasing the brilliance of the X-ray source. This is a consequence of Liouville's theorem, which states that phase space is conserved. Accordingly, focusing the beam to a smaller size by means of any diffractive or reflective optics will necessarily increase the flux density and the divergence of the X-ray beam, and *vice versa*. Additionally, any diffractive or reflective optics lose flux owing to their reflectivity, which usually is ≤90%. Apertures such as slits can help to reduce beam size and divergence, but only at the expense of flux.

Brilliance is more important than flux for experiments with small specimens (*e.g.* single crystals) or small regions of interest (*e.g.* microdiffraction), where it is generally desirable to work

references