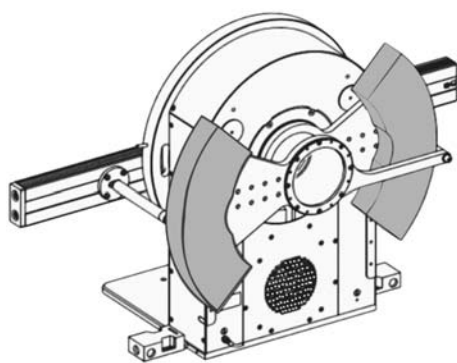


## 2.1. LABORATORY X-RAY SCATTERING

**Figure 2.1.10**

Example of counterbalancing of a vertical  $\theta$ – $\theta$  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  $\omega$ – $\theta$  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  $\omega$ – $2\theta$  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 ( $\omega$ ,  $2\theta$ ) 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  $\psi$  and  $\varphi$  axes of the specimen stage are mostly used for specimen orientation; the typical angular accuracy and precision are in the range of about  $0.01^\circ$ .

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  $10\ \mu\text{m}$ , and for a four-axis goniometer with a Eulerian cradle less than  $50\ \mu\text{m}$ ; 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  $0.01^\circ 2\theta$ , 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  $\alpha_I$ , 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

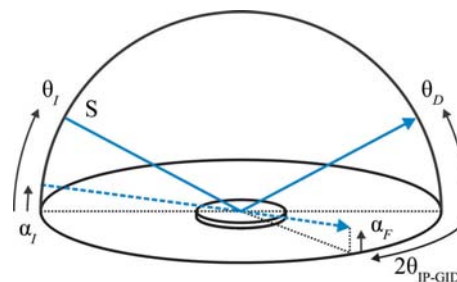
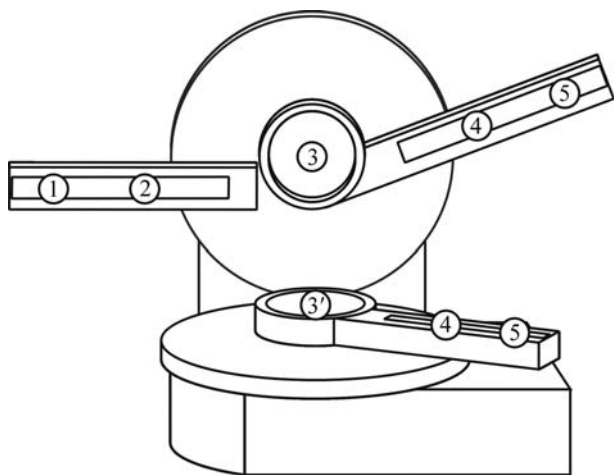
**Figure 2.1.11**

Illustration of coplanar and in-plane diffraction. S: X-ray source.  $\theta_I$ ,  $\theta_D$ : incident and diffracted beams for coplanar diffraction.  $\alpha_I$ ,  $\alpha_F$ ,  $2\theta_{\text{IP-GID}}$ : incident-beam angle, exit angle and diffracted-beam angle, respectively, for in-plane grazing-incidence diffraction.

## 2. INSTRUMENTATION AND SAMPLE PREPARATION



**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  $\alpha_F$ .

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  $90^\circ$  in  $\psi$ . As line focus is usually employed for IP-GID measurements, the X-ray source is also turned by  $90^\circ$  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  $\lambda$ , i.e.  $\Delta\lambda$  is equal to  $1/1000$  of  $\lambda$ . 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.  $\text{mm}^{-2}$ . 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.  $\text{mrad}^{-2}$ . 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  $\text{mm}^2$ . The unit is p.p.s.  $\text{mm}^{-2} \text{mrad}^{-2}$ . 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  $\leq 90\%$ . 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