2.1. Instrumentation for laboratory X-ray scattering techniques

A. Kern

2.1.1. Introduction

X-ray scattering techniques are among the most essential means of characterizing materials, as they are the most direct analytical methods for providing structural information for a material. In particular, X-ray powder diffraction has become one of the most important techniques in materials science, since many materials are first formed or are only available or used as powders or other polycrystalline forms.

The ever-increasing need for materials characterization, from basic research to industrial quality control, has led to a multitude of evolutionary and revolutionary instrument and application developments. In the past two decades, the capabilities and thus the range of application of laboratory X-ray diffractometers have increased exponentially.

The present chapter covers the full range of commonly used instrumentation for home-laboratory X-ray scattering analyses as detailed in Section 2.1.2, with the focus on powder diffraction. The scope is limited to recent and commercial designs, available off-the-shelf from the major manufacturers. Neither technologically obsolete nor niche instrumentation will be discussed. A short description of the history of X-ray instrumentation is given in Section 2.1.3, illustrating the significant technological advances made since 1985. Sections 2.1.4 to 2.1.7 describe the components of the diverse range of currently available home-laboratory X-ray powder diffractometers. The most important concepts are discussed here; for technological details the reader is referred to the original literature or to textbooks.

In order to maintain neutrality as well as timeliness, the use of brand names and photos of real equipment has been avoided.

2.1.2. Scope and terminology

An X-ray (powder) diffractometer is by definition an instrument for measuring X-ray diffraction phenomena (from powders), where 'diffraction' is defined as elastic, coherent scattering of X-rays from a crystal lattice (in the crystallographic literature, the terms 'diffraction', 'X-ray diffraction' and 'Bragg diffraction' are frequently used synonymously). In recent texts, a 'powder' is frequently defined as a 'solid containing small crystallites or particles that will flow when agitated' in accordance to the usual sense of the word in colloquial speech.

Such definitions for 'X-ray diffractometer' and 'powder' are problematic, as their scope is too narrow and arbitrarily limited. They are probably the result of the historical development of the methodology and the lack of interaction between groups representing different application areas, such as X-ray scattering, emission or absorption techniques. The application range and thus capabilities of today's instrumentation are neither comprehensively nor even appropriately described by their implicit limitation to measuring X-ray diffraction phenomena of crystalline solids in powdered form.

It is well known that scattering and thus interference phenomena will occur with any type of waves and obstacles, and are by no means restricted to X-rays or perfectly regular arrays of atoms exhibiting long-range order (X-ray diffraction). In general,

X-ray scattering can provide information on the arrangement of atoms or particles in materials with short-range order or no order at all, like gases, liquids and amorphous solids. For this reason it is obvious that X-ray diffractometers are intrinsically suited (and are actually used) for a wide range of X-ray techniques beyond X-ray diffraction as defined above. These techniques not only comprise X-ray scattering from any solids or liquids with any degree of order, but also X-ray absorption (radiography) or X-ray emission (XRF) techniques, see also Section 2.1.4.3. Consequently, the following terminology will be used throughout the remainder of this chapter:

A *sample* is the object or quantity of material to be investigated, while the *specimen* is the representative portion of the sample that is actually prepared and analysed. Specimen properties such as microstructure and packing density may differ from the properties of the sample as a result of specimen preparation. This must be taken into account for selection of the appropriate instrument configuration, data acquisition and evaluation.

A *powder* is defined in EN-1330-11 (2007) as a 'large number of crystallites and/or particles (*i.e.* grains, agglomerates or aggregates; crystalline or non-crystalline) irrespective of any adhesion between them' and thus can be a loose powder (in the sense of common language), a solid block, a thin film or even a liquid. An *ideal powder* is represented by a virtually unlimited number of sufficiently sized, randomly oriented and spherical crystallites.

The term *X-ray diffractometer* will refer to an instrument that, in principle, is capable of doing any of the X-ray techniques mentioned above, further detailed in Section 2.1.4.3. Instrument components will be described independently of applications, as they are not exclusive to any application area. Note that the term X-ray diffractometer also explicitly includes 'film cameras'. This is worth mentioning, as even recent texts still differentiate between (i) cameras, originally characterized by the use of X-ray films, and (ii) diffractometers, originally defined as an instrument derived from a camera in which the film had been replaced by a point detector. In principle, any so-called cameras and any diffractometers can be equipped with any type of today's point, linear and area detectors, so the former distinction between cameras and diffractometers, which arose from the historical development of X-ray instrumentation, is completely obsolete.

2.1.3. Historical overview

2.1.3.1. *From film cameras to diffractometers*

2.1.3.1.1. *Film cameras*

Powder diffraction analysis started with the development of simple film cameras, right after von Laue formulated his basic diffraction theory and the Braggs, father and son, laid down the foundations of crystal structure analysis, in the years 1912–1914. The first and simplest cameras were developed independently by Debye & Scherrer (1916) and Hull (1917), using a film to detect the scattered X-rays, with the instrument geometry termed 'Debye–Scherrer geometry'. The basic drawback of Debye–Scherrer cameras was their lack of resolution. Consequently,

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–

references