# Chapter 8.2. Laue crystallography: time-resolved studies

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## 8.2.1. Introduction

The term 'Laue diffraction' describes the process of X-ray scattering that occurs when a stationary crystal is illuminated by a polychromatic beam of X-rays. The process therefore differs from the now more conventional diffraction techniques in which a moving crystal is illuminated by a monochromatic beam of X-rays. Although Laue diffraction was widely used for structure analysis in the early days of crystallography by Pauling, Bragg, Wyckoff and others, by the 1930s it was superseded by arguably simpler and more readily quantifiable monochromatic techniques. With the advent of naturally polychromatic synchrotron sources in the 1970s, it was natural to (re-)examine the suitability of the Laue technique. The first synchrotron-based Laue experiments to be published appear to have been those of Wood *et al.* (1983) for a small inorganic crystal and of Moffat *et al.* (1984) for a macromolecular crystal; see also Helliwell (1984, 1985). These experimenters realized that the Laue technique afforded exposure times that were short even with respect to those obtainable with similar crystals at the same synchrotron source using conventional monochromatic techniques, and much shorter than those obtainable with laboratory X-ray sources. This advantage, along with the use of a stationary crystal, the large number of Laue spots evident in a single image and the clear distinction of the Laue spots from the underlying X-ray background, suggested that the Laue technique might be particularly applicable to time-resolved crystallography. In this form of crystallography, the total X-ray scattering from the crystal (both the Bragg scattering and the diffuse, non-Bragg scattering) varies with time as the position and/or extent of order of the atoms in the crystal changes in response to some structural perturbation.

It is one thing to propose that a venerable technique may be applicable to a new class of experiments; it is quite another to identify and overcome the complexities and disadvantages of that technique, and to demonstrate how experiments should be conducted and raw data accurately reduced to structure amplitudes. It took roughly 15 years and the efforts of many investigators before it could be stated that Laue crystallography is coming of age (Ren *et al.*, 1999).

The redevelopment of Laue diffraction has depended on three main advances: the use of very intense polychromatic synchrotron sources; the realization that the so-called energy-overlap or overlapping-orders problem in Laue diffraction was theoretically tractable, of limited extent and could be overcome experimentally; and the development of appropriate algorithms and suitable software to address the energy-overlap, spatial-overlap and wavelength-normalization problems. All are discussed below.

Since both Laue crystallography and its applications to time-resolved studies have recently been described at length, this article emphasizes only the key points and directs the reader to the primary and review literature for the details.

## 8.2.2. Principles of Laue diffraction

The principles of Laue diffraction have been reviewed by Amorós *et al.* (1975), Cruickshank *et al.* (1987, 1991), Helliwell *et al.* (1989), Cassetta *et al.* (1993), Moffat (1997), and Ren *et al.* (1999).

Assume that a stationary, perfect single crystal that diffracts to a resolution limit of $d^*_{\max}$ is illuminated by a polychromatic X-ray beam spanning the wavelength (energy) range from $\lambda_{\min}$ ($E_{\max}$) to $\lambda_{\max}$ ($E_{\min}$). All reciprocal-lattice points that lie between the Ewald spheres of radii $1/\lambda_{\min}$ and $1/\lambda_{\max}$, and within a radius $d^*_{\max}$ of the origin $O$ where $d^*_{\max} = 1/d_{\min}$, the resolution limit of the crystal, are in a diffracting position for a particular wavelength $\lambda$, where $\lambda_{\min} \leq \lambda \leq \lambda_{\max}$ and will contribute to a spot on the Laue diffraction pattern (Fig. 8.2.2.1). All such points diffract simultaneously and throughout the exposure, in contrast to a monochromatic diffraction pattern in which each point diffracts sequentially and briefly as it traverses the Ewald sphere. A Laue pattern may alternatively be thought of as the superposition of a series of monochromatic still patterns, each arising from a different wavelength in the range from $\lambda_{\min}$ to $\lambda_{\max}$.

Each Laue spot arises from the mapping of a complete ray (a central line in reciprocal space, emanating from the origin) onto a point on the detector. In contrast, each spot in a monochromatic pattern arises from the mapping of a single reciprocal-lattice point onto a point on the detector. A ray may contain only a single reciprocal-lattice point *hkl* with spacing $d^*$, in which case the corresponding Laue spot arises from a single wavelength (energy) and structure amplitude, or it may contain several

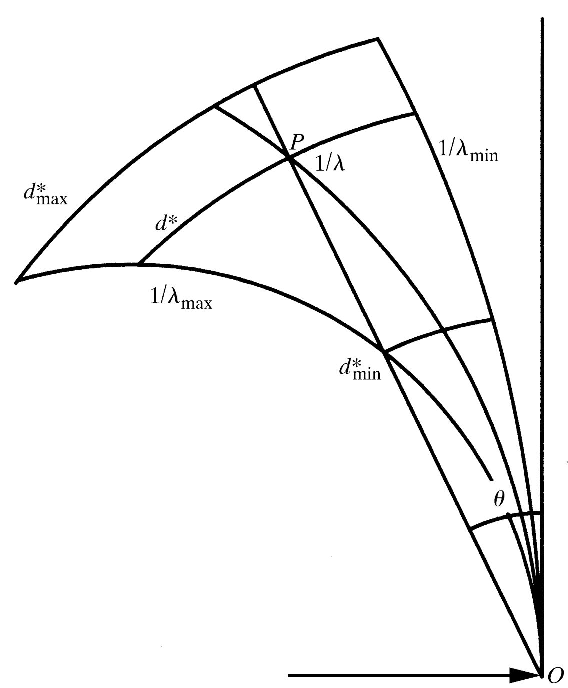


**Figure 8.2.2.1**
Laue diffraction geometry. The volume element d$V$ stimulated in a Laue experiment lies between $d^*$ and $d^* + \mathrm{d}d^*$, between the Ewald spheres corresponding to $\lambda$ and $\lambda + \mathrm{d}\lambda$, and between $\varphi$ and $\varphi + \mathrm{d}\varphi$, where $\varphi$ denotes rotation about the incident X-ray beam direction. The entire volume stimulated in a single Laue exposure lies between 0 and $d^*_{\max}$, between the Ewald spheres corresponding to $\lambda_{\min}$ and $\lambda_{\max}$, and between values of $\theta$ ranging from 0 to $2\pi$.



references