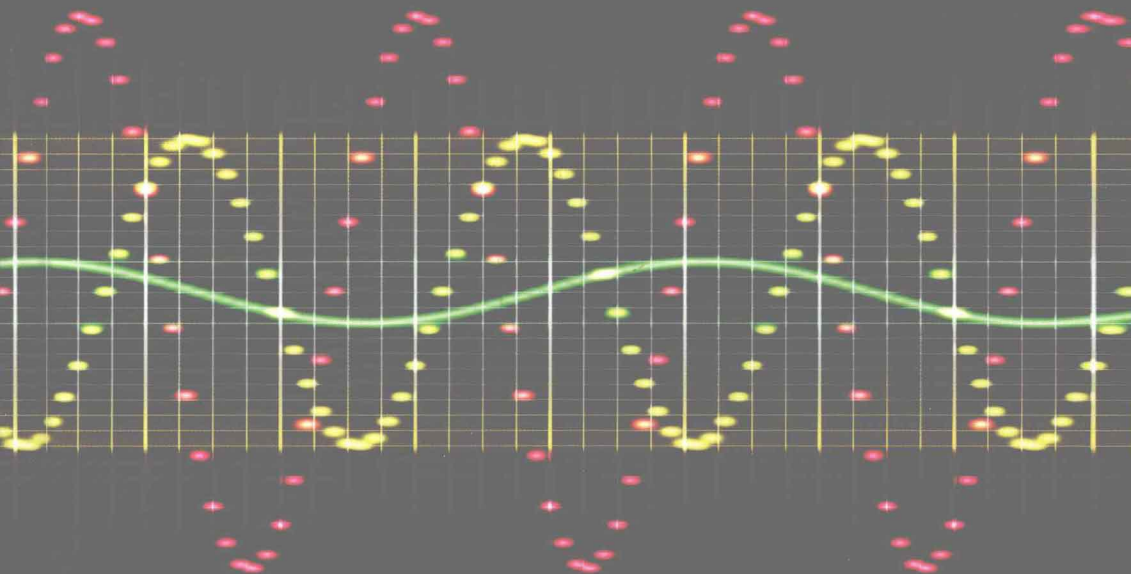


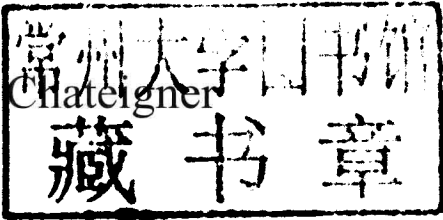


Combined Analysis

Daniel Chateigner

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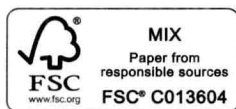
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Introduction

Recent developments in solid state chemistry and technology have made intensive structural analysis from single crystal diffraction a necessity. However, for many solids, single crystal growth is not easily undertaken and is sometimes impossible. When this is the case, or when structural defects cannot be overcome, the corresponding phases often have to be forsaken, due to the inherent difficulties of performing crystallographic characterization of polycrystals. Recently, powder diffraction techniques have progressed significantly, notably due to the Rietveld approach [RIE 69] and developments in computer science. Undoubtedly these developments are important in the study of solids that do not form large crystals, but also of all materials elaborated by classic solid state reactions, thin deposited structures, natural materials, such as clays, and more recently, nanomaterials in which the required properties are intimately linked to the stabilization of small crystals.

Since the publication of Rietveld's method, several tens of thousands of structures have been refined and thousands have been resolved *ab-initio* from only the diffraction data of powder samples. The number of laboratories and industries using this technique, which is still fairly new when dealing with the incorporation of various formalisms as used in the combined approach, continually increases.

However, materials with specific properties are often elaborated from low symmetry phases, which are consequently anisotropic. The optimization of a property is then conditioned by the elaboration processes, in which the intrinsic microscopic anisotropy of the constituting crystals has to be maintained at the macroscopic level. These elaboration techniques are complex (alignment under uniaxial pressure, magnetic or electric fields, thermal gradients, flux or substrate growing, etc., and combinations of these) and sample preparation is frequently complicated and time-consuming. Obviously, it is preferable that the process of sample characterization should be non-destructive. Unfortunately, when samples are

oriented, which was not often the case until recently, most of the characterization techniques (such as the Rietveld analysis of concerns here) require sample grinding. Very often this grinding is not acceptable, for the previously described reasons, but also in the case of rare samples (fossils, comets, etc.) or simply when grinding modifies the physical behavior of the samples themselves (thin films, residual stress materials, etc.). Sometimes grinding is simply not possible, imagine peeling off a 10 nm thick film from a substrate! In all these cases, combined analysis becomes essential.

The first chapter of this book is dedicated to some basic notions concerning diffraction by polycrystals. The various peak profiles used are described and for some of the most common combined analysis, the instrumental set-up is described in detail.

In the second chapter, powder diffraction data treatment is introduced. In particular, Rietveld analysis is detailed, including treatment of all the information provided by diffraction diagrams, in cases of samples not exhibiting texture, or with textures that are easy to treat.

The third chapter deals with automatic phase indexing, which is a necessary step that enables a structure to be elucidated *ab-initio*.

As its effect prevails on real samples where textures are often stabilized, quantitative texture analysis is detailed in the fourth chapter.

The fifth chapter is dedicated to microstructural aspects (isotropic and anisotropic crystal sizes and microdistortions) of the powder diffraction profiles.

In the sixth chapter, quantitative phase analysis from Rietveld analysis is introduced.

Chapter 7 describes residual stress analysis for isotropic and anisotropic materials.

Chapter 8 focuses on specular x-ray reflectivity and the various models associated with it.

Chapter 9 introduces the combined analysis concept, illustrating the difficulties encountered when we look at only one part of the analyses. Case examples are provided to illustrate the methodology.

Chapter 10 is dedicated to the anisotropic and tensorial macroscopic properties and their simulations to account for the distribution of crystallite orientations in samples.

This book does not intend to give the reader a complete description of the approaches provided, but is a basis for following the many concepts introduced over so many years, which are necessary to understand scattering patterns. Quantitative texture analysis is detailed in more depth than the other areas as texture appears to be the largest signal biaser.

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I am indebted to Magali Morales (CIMAP-Caen) who constantly comes with new issues, criticisms, advice and proposals. She was the first to test the Combined Analysis using the CPS detector set-up when taking part in the ESQUI European project. This work should be understood within hers.

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Chapter 1

Some Basic Notions About Powder Diffraction

1.1. Crystallite, grain, polycrystal and powder

A polycrystal, dealing with diffraction, is a solid substance divided into very small homogenous particles, elementary single crystals called crystallites (Figure 1.1). Crystallites are tridimensional domains which propagate an incident x-ray or neutron wave in a coherent way without phase loss. Crystallites are also called “coherent domains” in crystallography. A grain (such as the ones we can observe using a microscope for instance) can be made up of many crystallites or only a single crystallite. A single crystal is then composed of only one crystallite, and a polycrystal of an ensemble of crystallites.

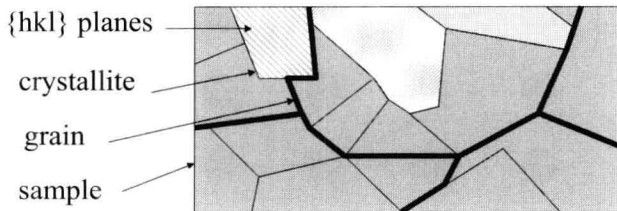


Figure 1.1. Definitions of grains (bold), crystallites (hatched zones) and crystallographic planes (hatchings) in a polycrystalline sample

A powder is an aggregate of crystallites (metal piece, ceramic, polymer or simply a compacted or not compacted powder) of varying number, shape, size and

crystalline state, it is thus a polycrystal. But an ideal powder or “standard”, again concerning diffraction experiments, is made up of a large number (several tens of thousands at least) of crystallites in a perfect crystalline state (without microdistortion or any other defects) which exhibit a very narrow monomodal size and shape distribution. Furthermore, the standard powder has crystallites which are randomly oriented to each other (without crystallographic texture). In such conditions, whatever the incident beam angle, the same volume fraction of crystallites always exist, oriented in such a way that they satisfy Bragg’s law (Bragg and Thomson, 1914), and are thus diffracted. Here we call “powder” the standard powder and polycrystal the regular powder.

1.2. Bragg’s law and harmonic reflections

1.2.1. Bragg’s law

This law establishes that a diffracted beam exists for a wavelength λ at an angle 2θ between the incident and diffracted beams (Figure 1.2), by the atoms lying in the $\{hkl\}$ planes at an interreticular distance d_{hkl} from one another, if the relation:

$$2d_{hkl} \sin \theta = n\lambda$$

[1.1]

is satisfied, in which n is the order of the reflection.

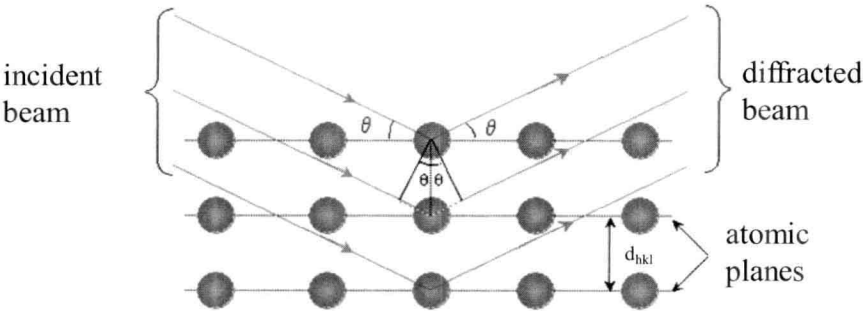


Figure 1.2. Schematic illustration of Bragg’s law