X-Ray Diffraction: A Practical Approach

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Preface

X-ray diffraction is an extremely important technique in the field of materials characterization to obtain information on an atomic scale from both crystalline and noncrystalline (amorphous) materials. The discovery of x-ray diffraction by crystals in 1912 (by Max von Laue) and its immediate application to structure determination in 1913 (by W. L. Bragg and his father W. H. Bragg) paved the way for successful utilization of this technique to determine crystal structures of metals and alloys, minerals, inorganic compounds, polymers, and organic materials—in fact, *all* crystalline materials. Subsequently, the technique of x-ray diffraction was also applied to derive information on the fine structure of materials—crystallite size, lattice strain, chemical composition, state of ordering, etc.

Of the numerous available books on x-ray diffraction, most treat the subject on a theoretical basis. Thus, even though you may learn the physics of x-ray diffraction (if you don't get bogged down by the mathematical treatment in some cases), you may have little understanding of how to record an x-ray diffraction pattern and how to derive useful information from it. Thus, the primary aim of this book is to enable students to understand the practical aspects of the technique, analyze x-ray diffraction patterns from a variety of materials under different conditions, and to get the maximum possible information from the diffraction patterns. By doing the experiments using the procedures described herein and following the methods suggested for doing the calculations, you will develop a clear understanding of the subject matter and appreciate how the information obtained can be interpreted.

The book is divided into two parts: *Part I—Basics* and *Part II—Experimental Modules*. Part I covers the fundamental principles necessary to understand the phenomenon of x-ray diffraction. Chapter 1 presents the general background to x-ray diffraction: What are x-rays? How are they produced? How are they diffracted? Chapter 2 reviews the concepts of different types of crystal structures adopted by materials. Additionally, the phenomena of diffraction of x-rays by crystalline materials, concepts of structure factor, and selection rules for the observance (or absence) of reflections are explained. Chapter 3 presents an overview of the experimental considerations involved in obtaining useful x-ray diffraction patterns and a brief introduction to the interpretation and significance of x-ray diffraction patterns. Even though the theoretical aspects are discussed in Part I, we have adopted an approach quite different from that of other textbooks in that we lay more emphasis on the physical significance of the phenomenon and concepts rather than burden you with heavy mathematics. We have used boxed text to further explain some particular, or possibly confusing, aspects.

Part II contains eight experimental modules. Each module covers one topic. For example, the first module explains how an x-ray diffraction pattern obtained from a cubic material can be indexed. First we go through the necessary theory, using the minimum amount of mathematics. Then we do a worked example based on actual experimental data we have obtained; this is followed by an experiment for you to do. Finally we have included a few exercises based on the content of the module. These give you a chance to apply further some of the knowledge you have acquired. Each experimental module follows a similar format. We have also made each module self-contained; so you can work through them in any order, however, we suggest you do Experimental Module 1 first since this provides a lot of important background information which you may find useful when you work through some of the later modules. By working through the modules, or at least a selection of them, you will discover what information can be obtained by x-ray diffraction and, more importantly, how to interpret that information. Work tables have been provided so that you can tabulate your data and results. Further, we have taken examples from *all* categories of materials—metals, ceramics, semiconductors, and polymers—to emphasize that x-ray diffraction can be effectively and elegantly used to characterize any type of material. This is an important feature of our approach.

Another important feature of the book is that it provides x-ray diffraction patterns for all the experiments and lists the values of the Bragg angles (diffraction angles, θ). Therefore, even if you have no access to an

x-ray diffractometer, or if the unit is down, you can use these 2θ values and perform the calculations. Alternatively, if you are able to record the x-ray diffraction patterns, the patterns provided in the book can be used as a reference; you can compare the pattern you recorded against what is given in the book.

This book is primarily intended for use by undergraduate junior or senior-level students majoring in materials science or metallurgy. However, the book can also be used very effectively by undergraduate students of geology, physics, chemistry, or any other physical science likely to use the technique of x-ray diffraction for materials characterization. Preliminary knowledge of freshman physics and simple ideas of crystallography will be useful but not essential because these have been explained in easy-to-understand terms in Part I.

The eight modules in Part II can be easily completed in a one-semester course on x-ray diffraction. If x-ray diffraction forms only a part of a broader course on materials characterization, then not all the modules need to be completed.

We realize that we have not included *all* possible applications of x-ray diffraction to materials. The book deals only with polycrystalline materials (mostly powders). We are aware that there are other important applications of x-ray diffraction to polycrystalline materials. Since this book is intended for an undergraduate course, and some special and advanced topics are not covered in most undergraduate programs, we have not discussed topics such as stress measurement and texture analysis in polycrystalline materials. X-ray diffraction can also be used to obtain structural information about single crystals and their orientation and the structure of noncrystalline (amorphous) materials. But this requires use of a slightly different experimental setup or sophisticated software which is not available in most undergraduate laboratories. For this reason we have not covered these topics.

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Part I
Basics

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X-Rays and Diffraction

1.1. X-RAYS

X-rays are high-energy electromagnetic radiation. They have energies ranging from about 200 eV to 1 MeV, which puts them between γ-rays and ultraviolet (UV) radiation in the electromagnetic spectrum. It is important to realize that there are no sharp boundaries between different regions of the electromagnetic spectrum and that the assigned boundaries between regions are arbitrary. Gamma rays and x-rays are essentially

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The Electron Volt

Materials scientists and physicists often use the electron volt (eV) as the unit of energy. An electron volt is the amount of energy an electron picks up when it moves between a potential (voltage) difference of 1 volt. Thus,

$$1 \text{ eV} = 1.602 \times 10^{-19} \text{ C (the charge on an electron)} \times 1 \text{ V} = 1.602 \times 10^{-19} \text{ J}$$

Although the eV has been superseded by the joule (J)—the SI unit of energy—the eV is a very convenient unit when atomic-level processes are being represented. For example, the ground-state energy of an electron in a hydrogen atom is −13.6 eV; to form a vacancy in an aluminum crystal requires 0.76 eV. The eV is used almost exclusively to represent electron energies in electron microscopy. The conversion factor between eV and J is $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$. Most texts on materials characterization techniques use the electron volt, so you should familiarize yourself with this unit.

The Ångstrom

The ångstrom (Å) is a unit of length equal to 10^{-10} m. The ångstrom was widely used as a unit of wavelength for electromagnetic radiation covering the visible part of the electromagnetic spectrum and x-rays. This unit is also used for interatomic spacings, since these distances then have single-digit values. Although the ångstrom has been superseded in SI units by the nanometer (1 nm = 10^{-9} m = 10 Å), many crystallographers and microscopists still prefer the older unit. Once again, it is necessary for you to become familiar with both units. Throughout this text (except in Experimental Module 8) we use the nanometer.

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identical, γ-rays being somewhat more energetic and shorter in wavelength than x-rays. Gamma-rays and x-rays differ mainly in how they are produced in the atom. As we shall see presently, x-rays are produced by interactions between an external beam of electrons and the electrons in

$h\nu$ [eV]	ν [Hz]	λ [nm]	Radiation
	— 10^{14}		infrared
— 1		— 10^3	visible
	— 10^{15}		
— 10		— 10^2	ultraviolet
	— 10^{16}		
— 10^2		— 10	
	— 10^{17}		
— 10^3		— 1	
	— 10^{18}		
— 10^4		— 10^{-1}	x-rays
	— 10^{19}		
— 10^5		— 10^{-2}	
	— 10^{20}		
— 10^6		— 10^{-3}	
	— 10^{21}		
— 10^7		— 10^{-4}	γ-rays
	— 10^{22}		
— 10^8		— 10^{-5}	

FIG. 1. Part of the electromagnetic spectrum. Note that the boundaries between regions are arbitrary. The usable range of x-ray wavelengths for x-ray diffraction studies is between 0.05 and 0.25 nm (only a small part of the total range of x-ray wavelengths).

the shells of an atom. On the other hand, γ-rays are produced by changes within the nucleus of the atom. A part of the electromagnetic spectrum is shown in Fig. 1.

Each quantum of electromagnetic radiation, or *photon*, has an energy, *E*, which is proportional to its frequency, ν:

$$E = h\nu \tag{1}$$

The constant of proportionality is Planck's constant *h*, which has a value of 4.136×10^{-15} eV·s (or 6.626×10^{-34} J·s). Since the frequency is related to the wavelength, λ, through the speed of light, *c*, the wavelength of the x-rays can be written as

$$\lambda = \frac{hc}{E} \tag{2}$$

where *c* is 2.998×10^8 m/s. So, using the energies given at the beginning of this section, we can see that x-ray wavelengths vary from about 10 nm to 1 pm. Notice that the wavelength is shorter for higher energies. The useful range of wavelengths for x-ray diffraction studies is between 0.05 and 0.25 nm. You may recall that interatomic spacings in crystals are typically about 0.2 nm (2 Å).

1.2. THE PRODUCTION OF X-RAYS

X-rays are produced in an x-ray tube consisting of two metal electrodes enclosed in a vacuum chamber, as shown in cross section in Fig. 2. Electrons are produced by heating a tungsten filament cathode. The cathode is at a high negative potential, and the electrons are accelerated toward the anode, which is normally at ground potential. The electrons, which have a very high velocity, collide with the water-cooled anode. The loss of energy of the electrons due to the impact with the metal anode is manifested as x-rays. Actually only a small percentage (less than 1%) of the electron beam is converted to x-rays; the majority is dissipated as heat in the water-cooled metal anode.

A typical x-ray spectrum, in this case for molybdenum, is shown in Fig. 3. As you can see, the spectrum consists of a range of wavelengths. For each accelerating potential a continuous x-ray spectrum (also known as the white spectrum), made up of many different wavelengths, is obtained. The continuous spectrum is due to electrons losing their energy in a series of collisions with the atoms that make up the target, as shown in Fig. 4. Because each electron loses its energy in a different way, a continuous spectrum of energies and, hence, x-ray wavelengths is pro-
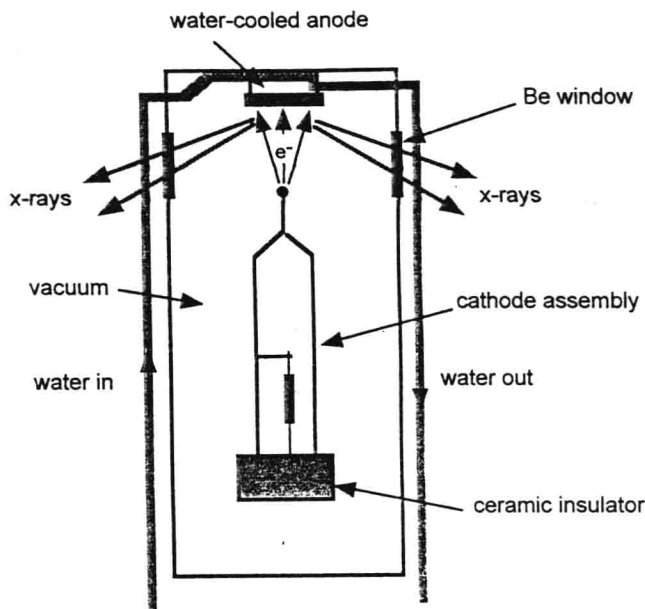
FIG. 2. Schematic showing the essential components of a modern x-ray tube. Beryllium is used for the window because it is highly transparent to x-rays.

duced. We don't normally use the continuous part of the x-ray spectrum unless we require a number of different wavelengths in an experiment, for example in the Laue method (which we will not describe).

If an electron loses all its energy in a single collision with a target atom, an x-ray photon with the maximum energy or the shortest wavelength is produced. This wavelength is known as the short-wavelength limit (λ_{SWL}) and is indicated in Fig. 3 for a molybdenum target irradiated with 25-keV electrons. [Note: When referring to electron energies, we use either eV or keV, but when referring to the accelerating potential applied to the electron, we use V or kV.]

If the incident electron has sufficient energy to eject an inner-shell electron, the atom will be left in an excited state with a hole in the electron shell. This process is illustrated in Fig. 5. When this hole is filled by an electron from an outer shell, an x-ray photon with an energy equal to the difference in the electron energy levels is produced. The energy of the x-ray photon is characteristic of the target metal. The sharp peaks, called *characteristic lines*, are superimposed on the continuous spectrum, as shown in Fig. 3. It is these characteristic lines that are most useful in x-ray diffraction work, and we deal with these later in the book.