
X-RAY STUDIES OF MATERIALS

A. GUINIER

*Service de Physique des Solides,
Faculté des Sciences, Université de Paris,
Orsay (S.-et-O.), France*

D. L. DEXTER

*University of Rochester,
Rochester, New York*

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Preface

During this century the investigation of the structure of matter has become increasingly detailed. Quantum mechanics and group theory have provided the necessary theoretical framework, while it is largely by X-rays that experimental determinations have been made possible.

In this tract we outline the current use of X-rays in the study of matter. There is necessary review of traditional techniques, but the aim is to describe the 'present state of the art.'

The level of presentation, in keeping with the policy of this series of tracts, is such that a beginning physics graduate student should be easily able to comprehend the contents. It is not intended for specialists or for workers in the field, but for people who know little about X-rays and would like to learn how they are being used today.

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Introduction

Our most direct knowledge of the universe comes to us through sight, i.e., by the use of electromagnetic radiation in the visible range, of wavelength about 5000 \AA . (We shall typically be dealing with characteristic lengths of the order $1 \text{ \AA} = 10^{-8} \text{ cm}$ to $1 \mu = 10^{-4} \text{ cm}$.) Our eyes, aided by optical instruments or other detectors, can discern details up to a limit related to the instrument's resolving power, which is a function of the wavelength of the radiation, λ . A consequence of diffraction theory is that specific structure of linear dimension much less than λ cannot be revealed by any optical instrument. In order to study matter on a very small scale, i.e., less than about 10^{-4} cm , it is accordingly necessary to use radiation of wavelength shorter than visible light, and ultraviolet microscopes are not uncommon as a step in this direction.

Below about 2000 \AA , however, and down to approximately 100 \AA , there are technical difficulties making it inconvenient to use these wavelengths as a tool. These difficulties are related to the circumstance that radiation of these frequencies is strongly absorbed by most materials, including air, and optical instruments, windows, sample holders, etc. are difficult to design and construct.

In practice, therefore, in the investigation of submicroscopic structure we are interested in the X-ray domain, which broadly extends from 0.1 \AA to 10 \AA . Towards longer wavelengths ("soft" X-rays), experimental difficulties are frequently encountered as a result of large absorption coefficients, and at

shorter wavelengths there are experimental problems connected first, with the high voltages that are necessary for the production of these "hard" X-rays and second, with the geometry required in the measurements. The wavelengths most commonly used are from 0.5 to 2 Å.

In comparison with visible light, X-rays have several properties of particular interest: (1) The wavelength is ~ 1000 to 10,000 times smaller (and the photon has an energy 1000 to 10,000 times greater). (2) X-rays have great penetrating power in matter. To cite an example of penetration depth, a beam of 0.7-Å X-radiation is reduced to half its initial intensity by 6 mm of carbon, 0.5 mm of aluminum, 15 μ of copper, and 6 μ of gold. (3) Further, whereas the absorption coefficient of a substance for visible light depends in a complicated way on the details of its structure, the absorption of X-rays is primarily a function of the constituents alone, and varies in a regular fashion with their atomic numbers.

Because of these characteristics, it is evident why X-rays can profitably be used in the study of the structure of matter. Their penetrating power is a most important property. It is obvious that if they were completely stopped by a superficial layer, they would not be able to disclose information about internal structure. Further, their wavelength is of the order of atomic dimensions and thus of the interatomic distance in a condensed state. Accordingly we may expect to utilize X-ray techniques to investigate the details of structure on the atomic scale. On the other hand, just as we use visible light to see objects much larger than the wavelength, so X-rays can be used to investigate objects much larger than atomic dimensions. In this case X-rays are useful because of their large penetrating power. Further, the energies of X-ray photons are comparable to the binding energies of the innermost electrons of the atoms, and in the quantum processes of emission and absorption they bear a close correspondence to the interior properties of the atom; this is in contrast to optical phenomena which are much more influenced by the atom's environment. Finally, because of

the high energy of the X-ray photon, of the order 10^4 electron volts, X-rays are useful in initiating internal processes in a solid involving high kinetic energy of outer electrons, e.g., in radiation damage studies.

The subject of this tract is to review the various applications of X-rays to the study of solids, with emphasis on modern techniques. We shall not go into technical details but shall stress physical mechanisms and the principles of different methods. Our goal is briefly to present to a physicist who is a non-specialist an idea of the results that he may expect to obtain by using X-rays in the problem that he is concerned with, in light of the present state of knowledge and technology. Furthermore, this physicist will find a concise description of the means of setting up a proposed experiment, as well as references to indispensable works which will give him technical details.

By way of introduction, we give a very brief survey of the general characteristics of the different techniques of observation of matter with X-rays.

1.1 Optical Images

This is the first technique that is thought of naturally in analogy with (visible) optics. Unfortunately, it is not very useful in the X-ray domain. The reflection and refraction of X-rays are rather different from these phenomena in the visible region, and are such as not to be well adapted to their use in "optical" instruments. For example, the index of refraction is typically unity within a few parts in a million. Consequently, hardly any optical instruments exist for X-rays. (Nevertheless, we shall cite various interesting attempts to construct an *X-ray microscope* based on total reflection of X-rays at very small angles.)

In the absence of traditional optical systems, we are reduced to a very rudimentary method of image formation by the *shadow method*. Everyone is familiar with the uses of radiography in medicine and for microscopic inspection of parts in industry. This technique has recently been perfected in regard to its

resolving power to give rise to *microradiography*, whose varied and interesting possibilities we shall discuss.

1.2 X-Ray Diffraction

The major part of this work will be devoted to this fundamental use of X-rays. Each atom exposed to a beam of X-rays is a source of a coherent scattered wave, which interferes with those emitted by neighboring atoms. The method consists of studying the spatial distribution of the total diffracted wave. The success of this method proceeds from the simplicity of the phenomena when the diffracting sample is a crystal. The experiments of von Laue, then of W. H. Bragg and W. L. Bragg in 1912 have shown that crystal structure, that is to say, the arrangement of the atoms, can be deduced from diffraction patterns. The developments of these techniques are considerable, and we shall show how X-rays can lead to results, sometimes astonishingly precise, on the atomic structure not only of "perfect" crystals but of real crystals with their accidental irregularities, and of amorphous solids, and of liquids as well.

1.3 X-Ray Spectroscopy

Recall the historic fundamental role that emission and absorption spectra have played in the determination of the energy level structure of electrons in the atom, dating from the early work of Moseley. More recently, X-ray spectroscopy has developed in two different directions. On the one hand, it is used as a means of analysis for the elements, frequently in conjunction with visible spectroscopy, because the two techniques are often complementary. On the other hand, very precise spectroscopy of X-rays has shown that certain details (slight line displacements and structure of absorption edges) depend on the structure of the solid in which the atom is bound, that is, depend on the local environment, and thus give information about the binding of matter. It is no longer a question of a geometric study of the *spatial* distribution of atoms, but rather a study of the *energy* distribution of electronic levels.

These are the three techniques of observation, very different in their application and their possibilities, which we group together in this volume because all three use the same X-radiation.

Reference

Ewald, P. P., *Fifty Years of X-Ray Diffraction*, International Union of Crystallography, 1962.

Production and Detection of X-Rays

2.1 X-Ray Tubes

X-rays are emitted when a beam of fast electrons collides with the surface of a solid. The customary X-ray tube is a sealed tube with a high vacuum containing a cathode source of electrons, e.g., a tungsten filament, and an anode, between which a voltage of 10 to 100 kV can be established. This voltage is maintained continuously, or may be replaced by an alternating voltage; in this event the tube is self rectifying and only emits X-rays during a half period so that the yield is not as good. Typical currents are of the order 10 to 25 ma, depending on the size of the focus.

The energy of the electron beam is mostly converted into heat in the anode. Thus it is common to use a water-cooled anode so that the tube can function continuously without having the anode deteriorate by sublimation. The power of an X-ray tube is limited by the rate of removal of the heat created at the focus. The most favorable conditions are with metals which are very good heat conductors, such as copper, or have high melting points, such as tungsten and molybdenum. In a typical case, with a focus for the electron beam of 1 to 5 mm², the maximum expendable power is of the order of 400 watts/mm² for copper and molybdenum, or 200 watts/mm² for cobalt or iron. The geometry of the tube is designed so that the incident electron beam is almost normal to the anode's surface, and the X-rays are viewed almost parallel to the surface. Thus the brightness of the source is augmented (in contrast with what happens for

visible light sources). For example, a focus of 2 mm diameter on the anode surface appears at a viewing angle of 6° as a line source ($0.2 \times 2 \text{ mm}^2$) (Fig. 2.1).

There is little progress to report or to be anticipated in the improvement in the intensity of normal tubes, but two interesting types of special tubes of great intensity have been developed.

1. *Rotating anode tube.* The rotation of the anode is such that the focus remains stationary in space but the liberated heat, distributed on a large surface, can be removed much more

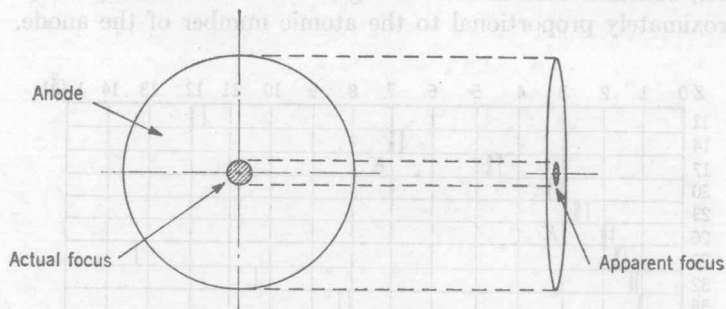


Fig. 2.1. Circular focus used at an emergence angle of 6° .

easily. The gain in power is about a factor of 10. The vacuum in the tube is maintained by a pump on account of the seals necessary for the rotation of the anode and the intake of the cooling water.

2. *Point-focus tube.* By a more or less complex optical electronic system, the electron beam is concentrated on the surface in a focus of the order of $(50 \mu)^2$. The removal of heat from such a point focus is relatively more efficient, and the power dissipation can reach 10 kW/mm^2 . But though the intensity per unit area of such a source is very strong, the total power emitted is much less than in a normal tube. A point-focus tube can be particularly useful, provided it is used in specially adapted mountings.

2.2 Spectral Distribution

X-ray tubes simultaneously emit two sorts of spectra: (1) continuous radiation (or *Bremsstrahlung*); (2) line radiation characteristic of the anode.

1. *The continuous spectrum* is electromagnetic radiation emitted by the electron during its decelerated motion as it is being stopped by the matter (whence the name *Bremsstrahlung*, or "braking radiation"). The spectral distribution depends only upon the operating voltage, and for given operating conditions (i.e., constant current and voltage), the total intensity is approximately proportional to the atomic number of the anode.

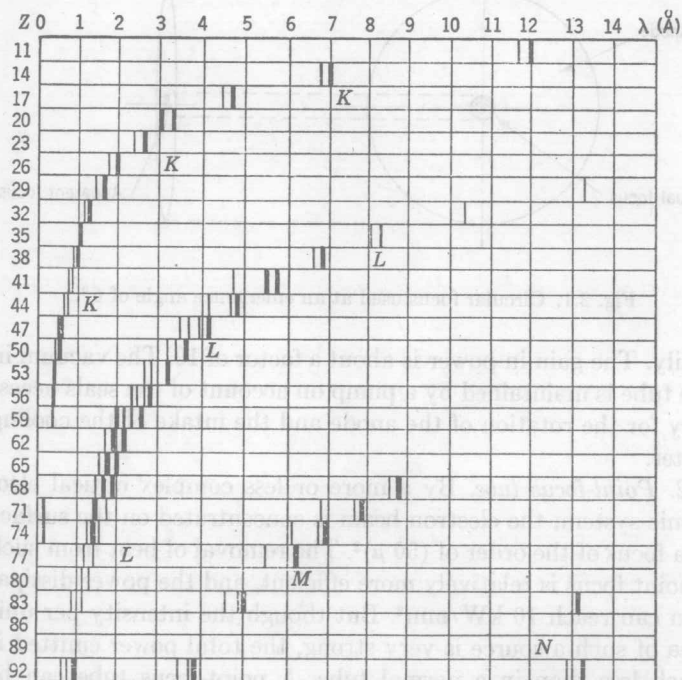


Fig. 2.2. Characteristic K, L ... line spectra of the elements of atomic number Z as a function of wavelength λ .

Therefore the continuous spectrum is very important for heavy elements (tungsten) and practically non-existent for light elements (aluminum). Its main property is starting suddenly at a minimum wavelength $\lambda_0 = 12400/V$ (in angstroms), where V is the operating voltage. There is a maximum of emission in the vicinity of $3/2 \lambda_0$; then the emission decreases as λ increases, principally because of absorption in the anode and in the windows of the tube. The continuous spectrum for a given anode is the more intense and the more abundant in short wavelengths, the higher the voltage of the tube. This is the source of "white" radiation which is necessary in certain techniques in crystallography and is the radiation used in high-voltage radiography.

2. *Characteristic radiation* corresponds to the emission of a photon during the transition of an electron to a lower level, when the atom has been ionized in an inner shell under the action of cathode rays. Characteristic X-radiation is classified into the K, L, M, \dots series corresponding to the various atomic levels, i.e., the principal quantum numbers. Wavelengths of homologous rays vary roughly as the inverse square of the atomic number (Moseley's law) (Fig. 2.2). A series of lines is only emitted if the voltage is greater than the ionization potential of the corresponding level (K, L, \dots). The most interesting line is the K_α line because it is well isolated and is the most intense (its intensity is very much greater than that of the adjacent continuous spectrum even in fairly heavy elements such as Ag). As a zero-order approximation, we can consider an X-ray tube operating at rather low voltage (25 kV) with anodes of not too heavy atomic weight (e.g., Cu), to be a monochromatic source of the K_α wavelength of the metal in the anode. In order to vary the wavelength, it is of course necessary to change tubes (or exchange only the anodes in demountable tubes).

Actually, the monochromaticity of the source is only approximate for three reasons:

1. There is a continuous spectrum superimposed.
2. There is another characteristic line, the K_β line, with a wavelength about 15% smaller than K_α . (The L lines are so far

removed in wavelength that they can usually be eliminated without difficulty by an absorbing filter.) Filters which suppress K_β can also be constructed, making use of discontinuities of K absorption (for example, 0.02 mm of Ni for a Cu anode, Zr for Mo, etc.); the filter absorbs most of K_β and little of K_α .

3. Finally, K_α is really a doublet formed of two lines, K_{α_1} and K_{α_2} , with an intensity ratio of 2:1, and a wavelength difference about 0.004 Å.

Table 2.1 gives the wavelengths of the characteristic lines used most often in crystallography.

Table 2.1 Characteristic K Radiation Wavelengths of Some Common Anodes

Anode element	Atomic number	Wavelength, angstroms		
		K_{α_1}	K_{α_2}	K
Chromium	24	2.294	2.290	2.085
Iron	26	1.940	1.936	1.757
Cobalt	27	1.793	1.789	1.621
Copper	29	1.544	1.540	1.392
Molybdenum	42	0.713	0.709	0.632
Rhodium	45	0.617	0.613	0.545
Silver	47	0.564	0.559	0.497

2.3 Absorption Coefficients

For the planning of an experiment as well as for the interpretation of its results, it is important to know the absorption of X-rays in matter. The mass absorption coefficient, μ , of a homogeneous substance is defined by the relation $I = I_0 e^{-\mu m}$, where I and I_0 are the intensities before and after traversing the sample of m grams per cm^2 .

For any substance, we can easily calculate μ from the table of absorption coefficients for the constituent elements as a function of the wavelength. To a very good approximation, the different elements in a compound have an additive effect, and their absorption coefficient is independent of the nature of the com-

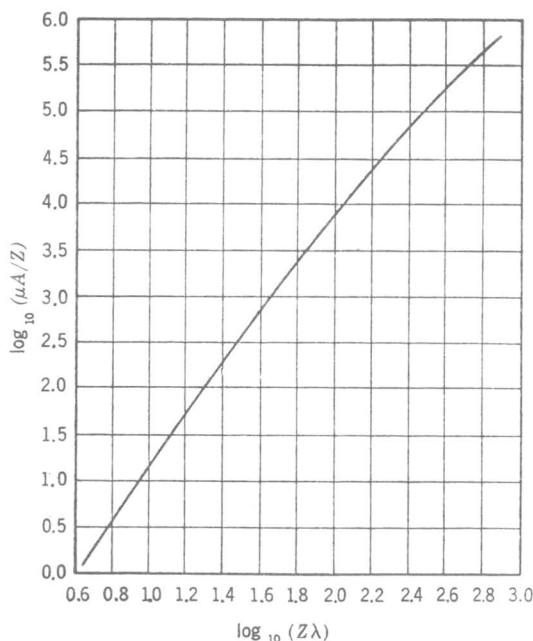


Fig. 2.3. Atomic absorption coefficient, μ_A/Z , as a function of the wavelength λ , the atomic number Z , and atomic mass of the absorbing element A . The curve gives directly the absorption coefficient for $\lambda < \lambda_K$. For $\lambda_K < \lambda < \lambda_L$ the number read on the curve must be multiplied by the ratio E_L/E_K of the energies of the electron in the L and K shells.

pound, except in the immediate vicinity of an absorption edge (see Chapter 9).

For a given element, there is a discontinuity of absorption when the wavelength passes the critical value at which the photon has enough energy to ionize a new shell. The most important discontinuity, λ_K , corresponds to the ionization of the K layer and causes an increase of absorption coefficient by a factor of about 6.

In a given domain ($\lambda < \lambda_K$, or $\lambda_K < \lambda < \lambda_L$, etc.), the absorption coefficient μ increases with λ as λ^3 . For a given wavelength

situated in the same domain for two elements, the ratio of absorption coefficients is approximately the cube of the ratio of atomic numbers. Figure 2.3 gives the absorption of the elements with an adequate approximation in many of the cases. The precise values are found in various tables (e.g., *International Tables for X-Ray Crystallography*, Vol. III).

2.4 Fluorescence Radiation

When X-radiation ejects an electron from a certain level, the excited atom falls again to the ground state in emitting characteristic X-rays. This is fluorescence radiation. Thus for iron, the absorption edge is $\lambda_K = 1.743 \text{ \AA}$: all wavelengths less than λ_K cause fluorescence radiation, comprising Fe K_α and Fe K_β principally, and also the weaker radiations of the L series.

The energy emitted in these lines is a considerable fraction of the energy absorbed (10–15%), and often constitutes the most important source of radiation scattered by matter; it makes possible the important application of spectrographic analysis (see Chapter 9). On the other hand, it is a great nuisance in crystallographic studies, and one should always endeavor to use an experimental beam such that fluorescence of the sample either doesn't occur or the principal fluorescence radiation is easily discriminated against by an absorbing film.

2.5 Detection of X-Rays

a. Fluorescent Screen. The simplest detector is a film containing a substance which emits visible fluorescent light when excited by X-radiation, e.g., ZnS, barium platinocyanide, etc. Fluorescent screens are used in radiography and for adjustment of crystallographic apparatus. However, they are not sensitive enough to detect low-intensity diffracted radiation. Image amplifiers can be used to increase the brightness so that the investigator need not work in the dark, but the detail observable is not increased.