CHARLES KITTEL

Introduction
to
Solid State
Physics

FOURTH EDITION

EXPERIMENTAL DIFFRACTION METHODS

The Bragg law (4) requires that $\theta$ and $\lambda$ be matched: x-rays of wavelength $\lambda$ striking a three-dimensional crystal at an arbitrary angle of incidence will in general not be reflected. To satisfy the Bragg law it is necessary to scan in either wavelength or angle. We do this experimentally by providing for a continuous range of values of either $\lambda$ or $\theta$, usually of $\theta$. The standard methods of diffraction used in crystal structure analysis are designed expressly to accomplish this. Three methods are employed, sometimes with elaborate modifications, in current research.

Laue Method

In the Laue method a single crystal is held stationary in a beam of x-ray or neutron radiation of continuous wavelength. The crystal selects out and diffracts the discrete values of $\lambda$ for which planes exist of spacing $d$ and incidence angle $\theta$ satisfying the Bragg law. The Laue method is convenient for the rapid determination of crystal orientation and symmetry. It is also used to study the extent of crystalline imperfection under mechanical and thermal treatment.

A Laue x-ray camera is illustrated schematically in Fig. 4. A source is used which produces a beam of x-rays over a wide range of wavelengths, perhaps from 0.2 Å to 2 Å. A pinhole arrangement produces a well-collimated beam. The dimensions of the single-crystal specimen need not be greater than 1 mm. Flat film is placed to receive the diffracted beams. The diffraction pattern consists of a series of spots, shown for a silicon crystal in Fig. 5.

Each reflecting plane in the crystal selects from the incident beam a wavelength satisfying the Bragg equation $2d \sin \theta = n\lambda$. The pattern will show the symmetry of the crystal: if a crystal with four-fold axis of symmetry is oriented with the axis parallel to the beam, then the Laue pattern will show the four-fold symmetry, as in Fig. 5. The Laue pattern is widely used to orient crystals for solid state experiments.

The Laue method is practically never used for crystal structure determination. Because of the wide range of wavelengths, it is possible for several wavelengths to reflect in different orders from a single plane, so that different orders of reflection may superpose on a single spot. This makes difficult the determination of reflected intensity, and thus the determination of the basis.
Figure 6 A rotating-crystal camera, with a crystal mounted on the rotating spindle. (By permission from *Structure of metals*, by C. S. Barrett.)

Figure 7 (a) Intensity versus wavelength distribution for x-rays from a Mo target bombarded by 20 keV electrons. (b) for the neutron beam emerging from a reactor with the wavelength band selected by a crystal monochromator. (After G. Bacon.)

Figure 8 Sketch of a monochromator which by Bragg reflection selects a narrow spectrum of neutron wavelengths from a broad spectrum incident beam. The upper part of the figure shows the analysis (obtained by reflection from a second crystal) of the purity of a 1.16 Å beam of neutrons from a calcium fluoride crystal monochromator. The peak intensity at 0.58 Å is less than 1 percent of that at 1.16 Å. The main beam is that not reflected from 20°.

Figure 9 A small rotating-crystal spectrometer at Harwell. The large can contains a neutron counter surrounded by shielding material. Most counters used in neutron diffraction studies are filled with boron trifluoride enriched in B10. (Courtesy of G. Bacon.)

2 Crystal Diffraction and the Reciprocal Lattice

Rotating-Crystal Method

In the rotating-crystal method a single crystal is rotated about a fixed axis in a beam of monoenergetic x-rays or neutrons. The variation in the angle θ brings different atomic planes into position for reflection. A simple rotating-crystal x-ray camera is shown in Fig. 6. The film is mounted in a cylindrical holder concentric with a rotating spindle on which the single crystal specimen is mounted. The dimensions of the crystal usually need not be greater than 1 mm. The incident x-ray beam is made nearly monochromatic by a filter or by reflection from an earlier crystal. The beam is diffracted from a given crystal plane whenever in the course of rotation the value of θ satisfies the Bragg equation. Beams from all planes parallel to the vertical rotation axis will lie in the horizontal plane. Planes with other orientations will reflect in layers above and below the horizontal plane.

The intensity distribution of the radiation from a 30 keV x-ray tube with a molybdenum target is shown by Fig. 7a. The distribution of neutrons emerging from a nuclear reactor is shown by Fig. 7b. If we reflect the x-ray or neutron beam from a monochromating crystal, as in Fig. 8, we get the crosshatched distribution of Fig. 7b. A simple rotating-crystal neutron spectrometer is shown in Fig. 9.

Several variations of the rotating-crystal method are in common use. In oscillating-crystal photographs the crystal is oscillated through a limited angular range, instead of being rotated through 360°. The limited range reduces the possibility of overlapping reflections. The Weissenberg goniometer and also the precession cameras shift the film in synchronism with the oscillation of the crystal. Modern methods use diffractometers in which scintillation counters or proportional counter tubes are used to detect the diffracted radiation. These
methods allow automatic collection of data: complex structures may exhibit 10,000 diffracted rays.

Nearly all crystals with simple structures were solved by x-ray analysis a long time ago. One present center of interest in x-ray structure analysis is in the determination of the configuration of enzymes with a molecular weight between 10,000 and 100,000. The crystallization of an enzyme and the subsequent x-ray analysis of the structure of the crystal is the most effective method for the determination of the shape of the molecule. The coordinates of 500 to 5000 atoms in a cell are wanted, so at least this number of x-ray reflection lines is required. Computer programs have enormously simplified the problem of structure determination.

**Powder Method**

In the **powder method** (Fig. 10) the incident monochromatic radiation strikes a finely powdered specimen or a fine-grained polycrystalline specimen contained in a thin-walled capillary tube. The distribution of crystallite orientations will be nearly continuous. The powder method is convenient because single crystals are not required. Diffracted rays go out from individual crystallites which happen to be oriented with planes making an incident angle \( \theta \) with the beam satisfying the Bragg equation. An early neutron powder spectrometer as used at Oak Ridge is shown in Fig. 11. Figures 12 and 13 are examples of powder-pattern results. Diffracted rays leave the specimen along the generators of cones concentric with the original beam. The generators make an angle 2\( \theta \) with the direction of the original beam, where \( \theta \) is the Bragg angle. The cones intercept the film in a series of concentric rings.

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**Figure 10** X-ray powder diffraction camera. The specimen is a polycrystalline powder. (Courtesy of Philips Electronic Instruments.)

**Figure 11** An early neutron spectrometer for powder studies, after E. O. Wollan and C. G. Shull, Phys. Rev. 73, 830 (1948). The sketch shows the monochromating crystal (detailed in left center) collimating slits, shielding, second spectrometer with location of powder specimen and counter.

**Figure 12** Neutron diffraction pattern for powdered diamond. (After G. Bacon.)
LAUE DERIVATION OF AMPLITUDE OF SCATTERED WAVE

The Bragg derivation of the diffraction condition gives a neat and clear statement of the condition for the constructive interference of waves scattered by point charges at the lattice points of a space lattice. When we are concerned with the intensity of scattering from a spatial distribution of electrons within each cell, we must carry out a deeper analysis. The simplest procedure (due to Laue) is to add up the contributions of the wavelets scattered from each volume element of the crystal. Another method of analysis, given in Advanced Topic A, looks for solutions of the electromagnetic wave equation in a medium with the dielectric constant a periodic function of position within the crystal.

The problem treated by Laue is to find the directions of the waves that leave a crystal, given the direction of the incident wave (Fig. 14). The final result is given in (20) and (22) below. We assume that the response of the crystal is linear, so that the frequency $\omega'$ of the diffracted wave generated by the response of the crystal is identical with the frequency $\omega$ of the incident wave. The magnitude of the wavevector of a wave in vacuum satisfies $\omega = ck$, so that if $\omega' = \omega$, then $k' = k$, where $k'$ is the magnitude of the wavevector of a diffracted wave in vacuum. To summarize,

$$\omega' = \omega ; \quad k' = k .$$  \hspace{1cm} (5)

We want to find the direction of a diffracted wave $k'$ in terms of the incident wave $k$ and of the primitive vectors $a$, $b$, $c$ of the crystal lattice.

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It is the real part of this expression that has physical meaning, but we can take the real part at the end of the calculation. This wave impinges on a scattering center at position $\rho$, and the response of the scattering center is to create a scattered wave. The form of the scattered wave is

$$E(x) = E_0 e^{ik \cdot x} ,$$  \hspace{1cm} (6)

where we have omitted an unimportant angular factor. The amplitude of the scattered wave is proportional to the amplitude (6) of the incident wave\(^5\) at $\rho$ this gives the factor $E(\rho)$, and $C$ is a constant of proportionality which involves

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\(^5\) We assume the crystal is small, so that to a first approximation we may neglect the attenuation of the incident wave within the crystal.