CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 51: X-Ray Diffraction Techniques

In the last lecture, three different ways in which experiments on X-ray diffraction can be performed were briefly introduced. We now consider the first method, known as the Laue technique. In this technique, the wavelength is varied while the Bragg angle θ with respect to the (hkl) planes is kept fixed. The incident beam strikes different (hkl) planes at fixed values of the Bragg angle θ.

In this configuration, the crystal is kept fixed; it is neither moved nor rotated. An incident X-ray beam impinges on the crystal, and for different (hkl) planes the incident beam makes specific angles, giving rise to scattered beams in various directions. The incident X-rays, it should be recalled, consist of white radiation, and therefore contain a continuous range of wavelengths. If one considers the X-ray spectrum of white radiation, the horizontal axis represents wavelength and the vertical axis represents intensity. There exists a minimum wavelength below which no X-rays are present; this is denoted as λ_{min} and is also referred to as the short-wavelength limit. One may arbitrarily define a maximum wavelength λ_{max}, beyond which the intensity becomes very small and scattered beams cannot be observed. Thus, the effective wavelength range lies between λ_{min} and λ_{max}.

One geometry associated with this method is that in which the X-ray beam passes through a thin crystal; this is known as the Laue forward reflection geometry. Another geometry is the Laue back-reflection geometry, in which the crystal is sufficiently thick that the incident beam cannot pass through it, and the lattice planes instead reflect the beam backward. In both cases, multiple scattered beams are produced.

This geometry can be understood in reciprocal lattice space. Consider a reciprocal lattice in which the reciprocal lattice points are represented as dots, and let O denote the origin of the reciprocal lattice. Two spheres of reflection are drawn, with centers denoted as A and B. These spheres are spheres of reflection with radius $1/\lambda$. Since the wavelength varies in the Laue technique, the smallest possible sphere has a radius $1/\lambda_{max}$, while the largest sphere has a radius $1/\lambda_{min}$. Between these two limiting cases, there exist many spheres of intermediate radii corresponding to wavelengths lying between λ_{min} and λ_{max}.

For a given wavelength, a scattered beam is obtained wherever a reciprocal lattice point lies on the corresponding sphere of reflection. For example, for the smaller sphere corresponding to λ_{max}, the incident beam direction is represented by the vector $\hat{s}_0/\lambda_{max}$. If a reciprocal lattice point, say P, lies on this sphere, then the vector $\bar{S}/\lambda_{max}$ joining the center of the sphere to that point represents a scattered beam direction, and the vector $\overline{OP}$ corresponds to a reciprocal lattice vector. Hence, a scattered beam is produced. Similarly, for the larger sphere corresponding to λ_{min}, scattered beams are obtained at other reciprocal lattice points, such as points Q, Q' , and P', which lie on that sphere.

All reciprocal lattice points lying in the volume between the smallest and largest spheres will lie on one or another sphere of reflection corresponding to some wavelength between λ_{min} and λ_{max}. Each such point will therefore satisfy the diffraction condition and produce a scattered beam. For instance, if a reciprocal lattice point R lies on a sphere of reflection centered at some point C, corresponding to a specific wavelength λ between λ_{min} and λ_{max}, then a scattered beam will be produced in the direction given by the unit vector $\hat{s}/\lambda$ for that wavelength. Consequently, a large number of scattered beams are observed in the Laue technique.

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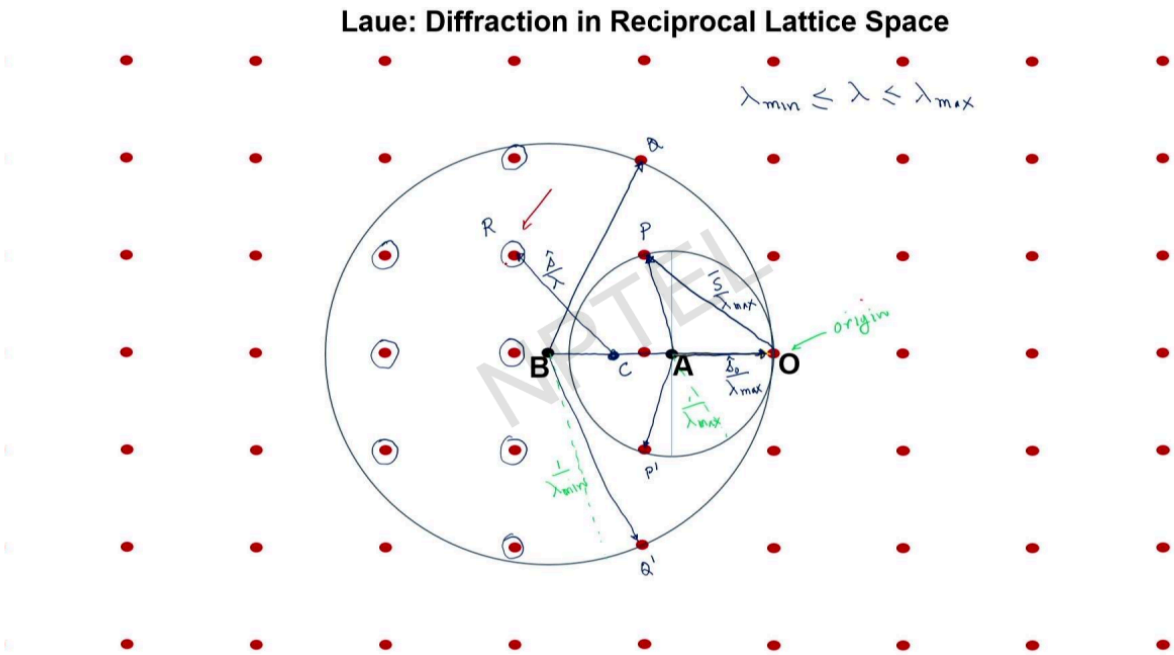

In practice, a recording medium is used to record the positions of these diffracted beams as spots. The resulting diffraction patterns are known as Laue diffraction patterns, with distinct patterns corresponding to forward Laue and backward Laue geometries. In the forward Laue pattern, groups of diffraction spots are observed to lie on ellipses, while in the backward Laue pattern, the diffraction spots lie on hyperbolas. Multiple such ellipses and hyperbolas can be identified in the respective patterns.

Although a detailed proof is not presented here, it can be stated that spots lying on ellipses in the forward Laue geometry and spots lying on hyperbolas in the backward Laue geometry arise from planes belonging to the same zone. To understand this, one may recall the zone weiss law, which states that a direction $[u\ v\ w]$ lies in a plane (hkl) if

$$hu + kv + lw = 0.$$

Spots belonging to the same zone correspond to planes that share a common direction, and this property assists in indexing the diffraction pattern.

Indexing refers to the process of associating Miller indices (hkl) with the individual diffraction spots, thereby identifying the lattice planes responsible for each reflection. Once indexing is completed, the Laue technique can be used, for example, to determine the crystallographic orientation of the crystal. It should be noted that the diffraction spots themselves correspond directly to reciprocal lattice points; thus, the diffraction pattern is effectively a representation of the reciprocal lattice. This illustrates the close relationship between diffraction and the reciprocal lattice.

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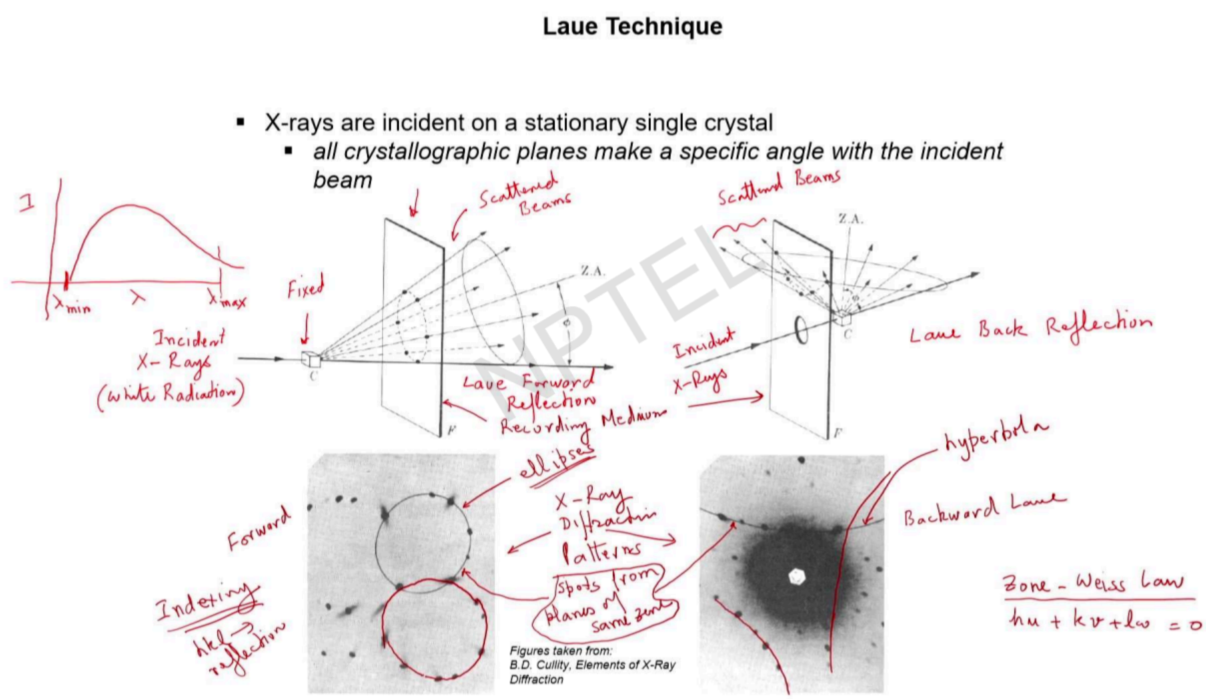

In practice, indexing Laue patterns is not straightforward, but the technique remains important as a method for crystal orientation determination. A second technique is the rotating crystal technique. In this method, monochromatic X-rays of a single wavelength are used, and the crystal itself is rotated. As a result of this rotation, the angle θ is varied, although not all possible values of θ are accessible. This technique can also be analyzed using the reciprocal lattice by considering a sphere of reflection, the incident beam vector $\hat{s}_0/\lambda$, and the origin of the reciprocal lattice.

When the crystal is rotated, the reciprocal lattice also rotates. For example, if a particular reciprocal lattice point is considered, it may intersect the sphere of reflection as the crystal rotates about a given axis. During this rotation, the point can intersect the surface of the sphere at various locations, resulting in scattered beams that form a conical surface. As the rotation continues, other reciprocal lattice points will also intersect the sphere at different locations, since the reciprocal lattice rotates together with the crystal. In this manner, several diffracted beams are produced in the rotating crystal technique.

A recording medium is used to capture the diffraction pattern obtained from this method. The pattern consists of discrete spots, where each spot corresponds to a reciprocal lattice point. These spots are observed to occur in layers. The appearance of layers arises from the rotation of the reciprocal lattice, which causes successive sets of reciprocal lattice points to satisfy the diffraction condition. For instance, a specific layer of spots can be identified on the recording medium, corresponding to a particular set of reciprocal lattice points. Using this technique, the structures of unknown crystals, particularly those with low symmetry, can be determined.

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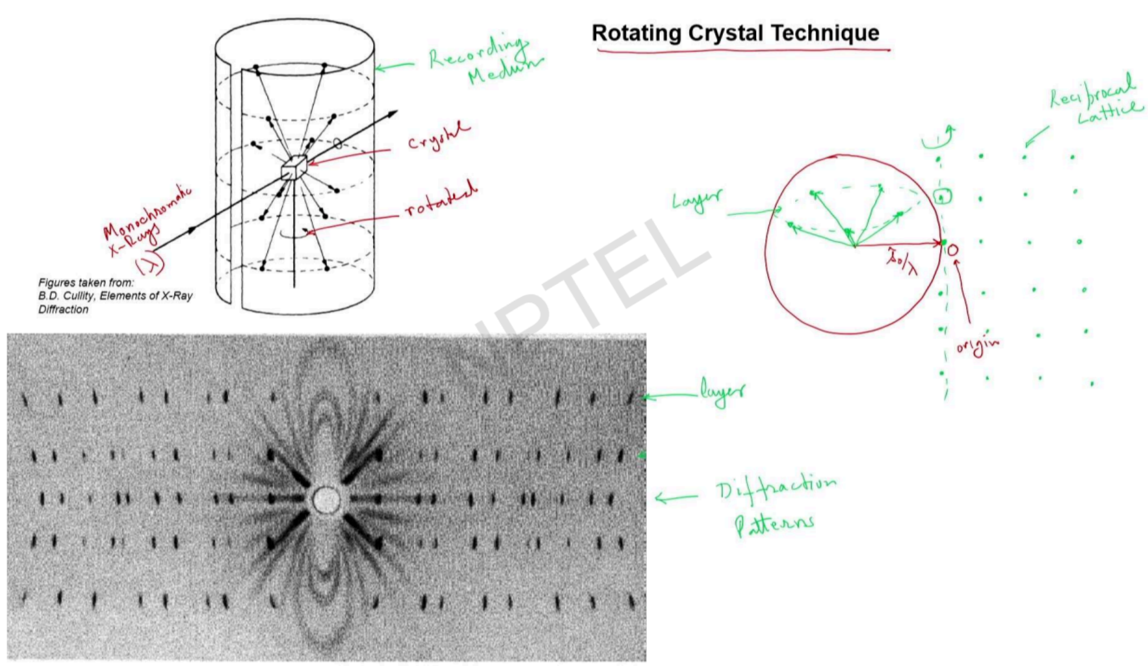

We now consider the third technique, which is the most widely used method and will be discussed in greater detail. This technique employs an X-ray diffractometer. In this instrument, monochromatic X-ray radiation is used. The setup consists of an X-ray source, a detector, and a sample placed between them.

Several geometries are employed in X-ray diffractometry. One may visualize a circle along which the X-ray source and the detector can move. In one geometry, the sample is placed at a fixed position, the source is located at one point on the circle, and the detector is located at another point. The incident beam strikes the sample at an angle θ with respect to the sample surface, and the reflected beam leaves the sample at the same angle θ.

One commonly used configuration is the 2θ geometry. In this geometry, the source is kept fixed, while the sample and the detector are rotated. The sample rotates about its own axis at the center, and the detector rotates along the circle. To ensure that the angle of incidence and the angle of reflection with respect to the sample surface remain equal, when the sample is rotated by an angle θ, the detector must rotate by an angle 2θ. This geometric arrangement guarantees that the incident and reflected angles are always the same. By rotating the system in this manner, different (hkl) planes can satisfy the Bragg condition, while the wavelength is kept fixed.

Another configuration is known as the θ–θ geometry. In this case, the sample is kept fixed, while both the source and the detector move by equal angles θ. Because both components move symmetrically, this arrangement is referred to as the θ–θ geometry.

In an X-ray diffractometer, the detector measures the intensity of the X-rays as a function of angle. The resulting diffraction pattern is a plot in which the horizontal axis is 2θ and the vertical axis represents the X-ray intensity. At specific values of θ, sharp intensity peaks are observed, corresponding to diffraction events. These peaks indicate the angles at which the Bragg condition is satisfied and no extinction occurs. The use of 2θ on the horizontal axis is largely a historical convention.

To understand this, consider a set of (hkl) planes, an incident beam, and a reflected beam. The incident beam makes an angle θ with the planes, and the reflected beam also makes an angle θ with the planes. If the incident beam is extended, the angle between the incident and reflected beams is 2θ. This angle is often referred to as the scattering angle, and it is this quantity that is recorded by the instrument. From the diffraction pattern, one obtains a series of values such as $2\theta_1$, $2\theta_2$, $2\theta_3$, and so on. These values are used to determine the crystal structure of the material, a procedure that will be discussed in a subsequent lecture.

A few remarks are necessary regarding the nature of the sample used in this technique. Typically, a polycrystalline sample is employed. A polycrystalline sample consists of many grains, each of which is a single crystal. These grains are randomly oriented with respect to one another. As a result, the (hkl) planes that are parallel to the sample surface differ from grain to grain. When monochromatic radiation is used, this random orientation allows different grains to satisfy the Bragg condition at different angles. Consequently, a wide range of incident angles with different (hkl) planes is effectively sampled, even though the wavelength is fixed.

Not all planes will satisfy the Bragg condition, and therefore not all orientations will produce reflections. Only those planes for which the Bragg law is satisfied at a specific angle will give rise to diffraction peaks. This is why the diffraction pattern consists of a series of discrete peaks, each corresponding to a particular set of (hkl) planes that satisfy the Bragg condition.

In the next lecture, the same diffraction pattern obtained from an X-ray diffractometer will be analyzed in detail to determine the crystal structure. Finally, one may observe the operation of the diffractometer itself, in which the source and detector move according to the $\theta - \theta$ geometry while the sample remains fixed, ensuring that the angles of incidence and reflection are always equal.

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