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The So-Called Correction of Bragg's Law

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Abstract

The traditional 'correction of Bragg's law' is discussed for any value of the refractive index of the diffracting medium. The finite angular range of reflection, as given by the dynamical theory of interference, is symmetrical about the corrected Bragg glancing angle only if absorption can be neglected. In this case the centroid of the reflected intensity is given by the corrected Bragg law. When absorption has to be taken into account or when, besides the surface-reflected ray, other strong diffracted rays occur inside the crystal, the simple corrected law is not sufficient. For spectroscopic work of precision equal to that achieved for visible light a careful analysis of the incident X-ray appears necessary concerning its collimation (angular width) and polarization. Furthermore, the setting of the diffracting crystal has to be investigated in order to avoid unwanted simultaneous reflections. The ideal would be to combine a recording of the actual reflection curve with the high-precision absolute measurement of the glancing angle that serves as zero for the reflection curve. This requires novel instrumentation.

1. A solitary ray: the refractive index

We write the periodic spatial part of the wave function as

$$\exp(2\pi i(\mathbf{kx})), \tag{1.1}$$

where $\mathbf{x}$ stands for the field point, $\mathbf{k}$ is the *wave vector*, $\mathbf{kx}$ signifies the scalar product of the two vectors, and the length of $\mathbf{k}$ is the *wave constant*

$$k = |\mathbf{k}| = 1/\lambda, \tag{1.2}$$

where λ is the wavelength.

A wave in free space has wavelength $\lambda_o = c/\nu$ (ν = frequency, c = velocity of light) and wave vector $\mathbf{k}_o$. Inside the medium a solitary X-ray has a phase velocity q, a wavelength $\lambda = q/\nu$, and wave constant

$$K = \nu/q = (c/q)k = nk, \tag{1.3}$$

where n is the *refractive index* of the medium, calculated by using the additive property of the 'optical density' according to the Lorentz–Lorenz relation

$$D = \frac{(n^2-1)}{(n^2+2)} = \frac{N(e^2/m)}{4\pi^2(\nu_0^2-\nu^2)}; \tag{1.4}$$

here, the sum is to be extended over all types of resonators; ν_o is the natural frequency and N is the number per unit volume of each sort of resonator.

For X-rays, n is very little different from 1 and usually smaller than 1, so that it is often convenient to write

$$n = 1 - \delta. \tag{1.5}$$

Wave vectors have dimension [1/length] and are therefore best visualized in reciprocal space. For solitary waves we construct two spheres about the origin of this space, one of radius k for waves propagating in empty space, the other of radius K for waves in the medium. Any allowed wave in either medium is represented by a wave vector beginning on the corresponding sphere and drawn into the origin of reciprocal space (point 1, Fig. 1). The sphere of radius K is the simplest example of the surface which, in more complicated cases, is called the *surface of dispersion.*

2. More than one diffracted ray inside the crystal

In order to find out whether an X-ray of wave vector $\mathbf{k}_1$ is a solitary beam, or is inseparable from rays of other directions, we use the primitive Laue theory in which all waves are assumed to have phase velocity c. We construct a sphere of radius k_o so that it touches the origin. The vector from the center to the origin is $\mathbf{k}_o$, the wave vector of the primary wave. If the sphere passes through other points of the reciprocal lattice, say points $h_1, h_2, h_3, \ldots$, then the radii to these points are wave vectors which are inseparably connected to the primary vector. In this case a bundle of waves is the optical field, the propagation of which is studied in the dynamical theory. If there are secondary rays, the refractive index discussed in the previous paragraph can no longer be considered a property of the

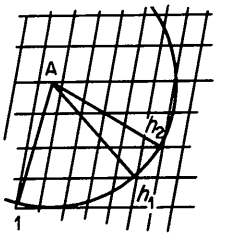

Fig. 1. The reciprocal lattice and the simultaneous wave vectors, with the sphere of reflection.

* See preceding Editorial.

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medium; instead, each ray has its own refractive index, and this varies rapidly with its direction.

3. Two beams: geometrical theory corrected for refraction in Bragg reflection

Assume that besides the origin, 1, only one lattice point, h, lies on the sphere of reflection. As long as this condition holds it entails rotational symmetry about the direction of $\mathbf{h}$ as axis. It is therefore sufficient to consider the meridional plane which contains $\mathbf{K}_1$ and $\mathbf{K}_h$. In Fig. 2, circles of radius k and K are drawn about the points 1 and h, such that $K/k = n$, where n is the refractive index of a solitary wave. Any wave vector of a wave in the interior of the medium starts on the K circle (the smaller one in the case of X-rays). The intersection of the k circles is called the *Laue point, La*; that of the K circles, the *Lorentz point, Lo*. The condition for obtaining two strong rays exists only in the interior of the crystal and the waves are represented by the vectors $Lo \rightarrow 1$ and $Lo \rightarrow h$. The 'reflecting' planes are normal to $\mathbf{h}$ and the angle between either of the vectors and the symmetry line of the figure is the *internal glancing angle*, θ. Since $|\mathbf{h}| = p/d$, where d is the spacing of the reflecting planes and p is the order of reflection, we see from the figure that

$$\sin\theta = \tfrac{1}{2}h/K \quad \text{or} \quad \lambda = 2(d/p)\sin\theta, \tag{3.1}$$

which is Bragg's law.

We do not observe the waves inside the crystal and must therefore express this condition in terms of the observable quantities outside, which will be denoted by the suffix 'o'. The condition of refraction (*Snell's law*) states that internal and external waves keep in step along the surface, that is, their wave vectors have the same component along the surface. We therefore draw a line parallel to the vector $\mathbf{h}$ through Lo and find its intersection with the circle of radius k_o. Connecting this point to the origin shows the vector $\mathbf{k}_o$ of the external wave, where $\mathbf{k}_o$ and the normal to $\mathbf{h}$ form the *observable external glancing angle* θ_o. If we naively apply Bragg's law to this glancing angle, given the order vector $\mathbf{h}$, we find a fictitious wave vector $\mathbf{k}_f$ which has the same direction as $\mathbf{k}_o$ but ends on the symmetry line of the figure.

We wish to find $\mathbf{k}$ in terms of θ_o, $\mathbf{h}$, and $\mathbf{n}$. From the figure we obtain the following relations:

$$K = nk \tag{3.2}$$

$$K\cos\theta = k\cos\theta_o \tag{3.3}$$

$$K\sin\theta = \tfrac{1}{2}h = k_f\sin\theta_o \tag{3.4}$$

$$(K)^2 = (\tfrac{1}{2}h)^2 + k^2\cos^2\theta_o = k_f^2\sin^2\theta_o + k^2\cos^2\theta_o. \tag{3.5}$$

Therefore

$$k^2(n^2 - \cos^2\theta_o) = k_f^2\sin^2\theta_o \tag{3.6}$$

or, in wavelengths,

$$\lambda_o^2 = \lambda_f^2(n^2 - \cos^2\theta_o)/\sin^2\theta_o. \tag{3.7}$$

This equation expresses the wavelength in vacuum, λ_o, in terms of the fictitious wavelength, λ_f, obtained by applying the uncorrected Bragg law to the glancing angle observed on the spectrograph. Relations (3.6) and (3.7) hold for all values of the refractive index n. It is true for $n < 1$ (X-rays) as well as for electrons with $n > 1$, or for visible light in iridescent media. Knowing the order of diffraction h, the wavelength *in vacuo* and the external angle, θ_o, we determine from (3.6)

$$n^2 = \cos^2\theta_o + (\tfrac{1}{2}h/k)^2 = \cos^2\theta_o + (\tfrac{1}{2}h\lambda_o)^2. \tag{3.8}$$

If the refractive index is very close to 1, writing $n = 1 - \delta$ and keeping only the lowest power in δ, we have

$$\lambda_o = \lambda_f(1 - \delta/\sin^2\theta_o), \tag{3.9}$$

a relation Stenström derived in 1919.

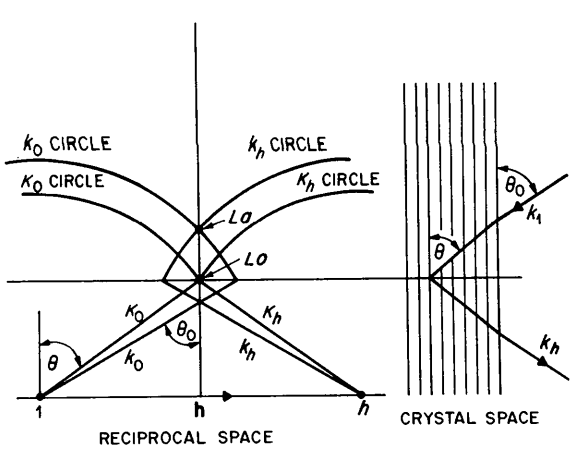

Fig. 2. The Bragg case; wave vectors in reciprocal and crystal space.

4. Two beams in transmission: symmetrical Laue case

This case is represented in Fig. 3. The internal and external wave vectors have automatically the same component along the crystal surface and there is no fictitious wave vector. Bragg's law holds for the observable quantities without correction.

5. Two beams: dynamical theory

According to the dynamical theory, strict compliance with the Bragg law is not required. Instead, a strong secondary beam is generated from a primary one over a small but finite range of angles of incidence. If the primary beam is incident on, and reflected by, the same face of a crystal as in the usual X-ray spectrometer, theory predicts for a non-absorbing crystal a range of several seconds of arc throughout which

an incident ray will be totally reflected. This range is centered on the corrected glancing angle of the geometrical theory. It is flanked, for slightly smaller and greater angles of incidence, by regions of '*Pendellösung*' within which the output drops off rapidly while oscillating between maxima and minima. The entire intensity of the secondary beam, plotted as a function of the glancing angle of the incident beam, *i.e.* the *reflection curve*, is symmetrical about the corrected Bragg angle provided absorption is neglected. The geometrical theory thus leads to the correct wavelength if we assume the glancing angle θ_o to be determined by the centroid of intensity of the (unresolved) line.

In an absorbing crystal, on the other hand, the reflection curve is not symmetrical. Fig. 4 (adapted from a paper by Renninger, 1975) shows the reflection curve for the 422 reflection from a silicon crystal in the Bragg case. The theoretical curve for a strictly plane incident wave has been convoluted with the angular distribution within the ray delivered by the monochromator which shows a spread of 1·1″. This procedure smooths out the *Pendellösung* variations of the reflected intensity. On account of the absorption coefficient (146 cm^{-1}) the curve is no longer symmetrical about the corrected Bragg angle; its centroid is shifted towards smaller angles, that is, the correction discussed so far is too large. The region of total reflection, between ±2″, is indicated in the figure.

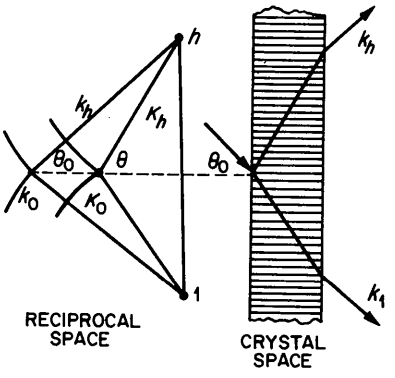

Fig. 3. The Laue case.

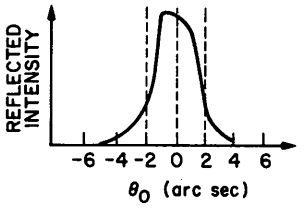

Fig. 4. Reflection curve for absorbing crystal. For the nonabsorbing crystal, total reflection occurs between the dotted lines.

It is true that in X-ray spectroscopy the angular width of the incident beam is much larger than 1·1″ and that therefore the process of convolution would wipe out much of the asymmetry in the recorded lines. But if comparisons of X-ray wavelengths are to achieve the accuracy of those of visible light, then the shape of the reflection curve will have to be taken into account.

6. Influence of simultaneous reflections

It can easily happen that apart from the main reflection of order h further secondary rays of orders h_1, h_2, ... are produced, unnoticed by the spectroscopist. This is the more likely the shorter the wavelength. In rotating the diffracting crystal about the normal to the reflecting planes, there may be a few azimuths for which no third beam is generated. In publications of spectroscopic research, little attention has been given to the complete setting of the crystal.

As long as only two rays exist, the cross section of the surface of dispersion is a simple hyperbola for each mode of polarization (say, for the electric vector normal to the plane of the rays). The distance between the vertices of the branches, or sheets of the hyperbolae, determines the width of the region of total reflection, and the central line between the branches gives the deviation from the uncorrected Bragg law.

With the appearance of a third ray, the two-sheet surface is deformed by a third sheet, the details depending on the geometry. Besides, if the beams are not coplanar, the polarization cannot be split in a simple manner; a surface of dispersion consisting of six sheets has to be considered. In a simple case when the third ray lies in the symmetry plane between the first two, this surface has been studied by Ewald & Héno (1968) and Héno & Ewald (1968) with the object of discussing the absorption of the wave fields and, in particular, of accounting for the enhanced Borrman effect. The influence of a third ray on the reflection curve of the first two cannot be determined in general but is not a difficult job for a computer, given the exact data of an experimental case.

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