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CORRECTION OF THE EXPRESSION OF THE INTEGRAL DIFFRACTION INTENSITY FOR CERTAIN TYPES OF X-RAY STRUCTURAL ANALYSIS METHODS

Florina Violeta ANGHELINA, Ileana Nicoleta POPESCU, Carmen POPA, Dan Nicolae UNGUREANU, Ion Florin POPA

Valahia University of Targoviste, Faculty of Materials Engineering and Mechanics
Aleea Sinaia, Nr. 13, 130004 Targoviste, Dambovita

E-mail: vianghelina@yahoo.com

Abstract: *Diffraction techniques and methods with X-rays and less diffraction of electrons, neutrons, etc. are frequently used to investigate the fine structure. X-ray techniques have the advantage that they are cheaper and provide statistical information at the level of fine ordered structure and are not significantly disturbed by the magnetic state of the substance. But the experimental reality complicates matters. The geometric divergence (vertical and horizontal) of the incident beam, the deviation from the ideal monochromatism and the diffraction geometry induce certain corrections for the expression of the integral diffraction intensity. This article addresses the calculation of the integral diffraction intensity affected by these factors for certain methods of X-ray structural analysis.*

Keywords**:** *X-rays, diffraction geometry, divergence parameters, Lorentz factor.*

1. INTRODUCTION

Metallic materials for mechanical applications (constructions, parts, prostheses, etc.) are materials characterized, in general, in terms of structure and composition and, as far as possible, by standardized quantitative methods. The use of standardized methods limits the uncertainty budget of the test, but does not ensure the minimum uncertainty [1,2,3,4,5].

Thus, although it seems contradictory, any standardized method leaves room for research on improving the quality of results as well as research on extending the scope of the method. Even if the field does not seem to be spectacular in scope of the scientific approach, it is still spectacular in terms of practical results, such as reducing costs, minimizing operating risks, improving the mathematical model of the measurement, estimating the uncertainty budget, etc.

2. THEORETICAL PRESENTATION

Techniques and methods of diffraction with X-rays and less diffraction of electrons, neutrons, etc. are frequently used to investigate the fine structure. X-ray techniques have the advantage that they are cheaper and provide statistical information at the level of fine ordered structure and are not significantly disturbed by the magnetic state of the substance.

Only the electric field counts for X-ray diffraction in crystals. It is dominant in the interaction with electrons and is also the field through which the amount of diffracted X-rays is measured, so the intensity of the diffraction line. [6,7,8]. According to the second principle of mechanics, then for the electron in the electric field of the incident wave it results:

$$eE_o \sin(\omega t) = m\, d^2z_e/dt^2 \quad (1)$$

e - electron charge, m - electron mass, ω - Eo 's pulsation
Solution of equation (1) is:

$$z_e = (-eE_o/m\omega^2)\sin(\omega t) \quad (2)$$

respectively the induced dipole is:

$$p_z = -ez_e = (e^2/m\omega^2)\,E_o \sin(\omega t) \quad (3)$$

The expression of the delayed dipole is:

$$[p] = [p_z] = -ez_e = (e^2/m\omega^2)\,E_o \sin(\omega(t - R/c)) \quad (4)$$

and c represents the speed of light.

Taking into account the expression of [**p**] the intensity of the electric field becomes:

$$E_\theta(R,\theta,t) = -\frac{e^2}{4\pi\varepsilon}\cdot\frac{1}{mc^2}\frac{1}{R}E_0 \sin\theta \sin\omega(t - R/c) \quad (5)$$

The expression for E_θ given by relation (5) is the basis for the development of the kinematic theory of X-rays. The term time does not play an important role because it disappears when calculating the average diffracted intensity $I_e = \langle E^2_\theta \rangle$. For the reasons shown, it is customary for E_θ's expression to be written as:

$$E_\theta(R,\theta,t) = -\frac{e^2}{4\pi\varepsilon}\cdot\frac{1}{mc^2}\cdot\frac{1}{R}E_0 \sin(\theta)\cdot e^{i\omega(t - R/c)} \quad (6)$$

i - represents the imaginary complex number (i^2=-1).

According to studies in the literature [9] the intensity of X-rays at point R is considered to be:

$$I_e(R,\theta)= E_\theta E^*_\theta =(\frac{e^2}{4\pi\varepsilon}\cdot\frac{1}{mc^2})^2\frac{1}{R^2}\sin^2(\theta)E^2 = (\frac{e^2}{4\pi\varepsilon}\cdot\frac{1}{mc^2})^2\frac{1}{R^2}\sin^2(\theta)I_0 \quad (7)$$

and E^*_θ is the complex conjugate of E_θ, Io is the intensity of the incident X radiation.

According to studies in the literature [10,11], the intensity diffracted by a crystallite, which is irradiated with the unpolarized monochromatic beam in the $\vec{u}$ direction will have the expression:

$$I_c(\vec{s}) = I_e(0)\frac{1+cos^2 2\theta}{2}\cdot F^2(\vec{s})\cdot G^2(\vec{s}) \quad (8)$$

considering $\vec{s}=\frac{\vec{u}-\vec{u_0}}{\lambda}$; $\vec{u_0}$ - direction of the incident beam;

$\vec{u}$ - direction of the diffracted beam;

$I_e(0)$ is the intensity of the incident beam ;

The term $\frac{1+\cos^2(2\theta)}{2}$ = p (2θ) is the polarization factor,

F ($\vec{s}$) is the structure factor, and

G ($\vec{s}$) is the interference function.

To define the factors that characterize the coherent scattering of X-rays ([10,11]), it was considered that the incident beam is a parallel and monochromatic plane beam. In real experience there have always been a number of practical limitations to the possibilities of achieving these conditions [6].

The following factors such as: the geometric divergence (both vertical and horizontal) of the incident beam, the deviation of the beam from the ideal monochromatism as well as the diffraction geometry lead to a further widening of the maximum of the observable diffraction. This additional enlargement usually far exceeds the enlargement resulting from the expression of $G^2(\vec{s})$ in relation (8).

That is why it becomes imperative to find and introduce a "geometric" factor that corrects the calculated value of the intensity for "real" conditions of a specific experience for a certain type of structural analysis. In the following paragraphs we will discuss the "geometric factor" in case we have defined the integral intensity diffracted by a crystalline plane.

3. METHOD PRESENTATION

Figure 1 shows a section of the Ewald sphere with the node hkl in reciprocal space, depending on the xy plane and the shape of the corresponding reflection hkl, on a diffractogram.

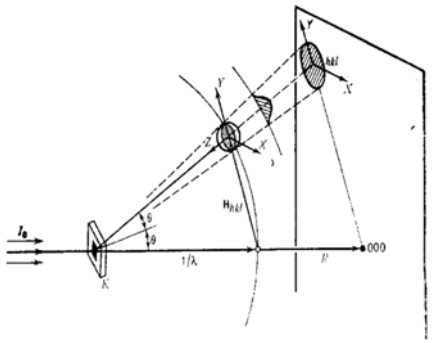


Figure 1. Scheme of diffraction geometry and detection geometry for a node on the Ewald sphere [12]

For crystals with 10^3 cells in a given direction, the maximum deviation of the direction of the diffracted radius from the $\overrightarrow{u_H}$ direction is about $0{,}02^0 \approx 1{,}2'$. In this case the "opening" at 1 m of the diffracted beam is about 10 mm.

Since diffracted radiation measuring devices (detectors) have a significant width of the window through which X-rays enter, it is clear that the detector simultaneously records X-rays which have the directions $\vec{u}$ contained in the solid angle of the detector, seen from the center of the corresponding crystal and with the center of the Ewald sphere.

Figure 1 assumes that the solid angle associated with the detector includes the solid angle below which the node is visible. In this case the intensity that is measured by the detector represents an integral intensity associated with all vectors whose vertices are on the surface Σ_0. This area results from the intersection of the Ewald sphere and the domain node H, denoted $I_{\Sigma 0}$, respectively:

$$I_{\Sigma 0} = \iint_\Omega I_c(\vec{u})d\Omega = \iint_\Omega dI_0(\overrightarrow{u_{r0}})g(\vec{s})\,G^2(\vec{s})d\Omega_0 \quad (9)$$

It is considered that there is a specific geometric divergence of the incident beam if it is assumed that the beam is a rigorous parallel plane, but the crystal rotates relative to the axis of the beam [6].

Horizontal divergence, but also vertical divergence has the main contribution to the spatial distribution of scattered radiation. They change the expression of the integral intensity generated by a crystallite.

Next we will deduce the expression of the Lorentz factor, necessary to correct the calculated value of the intensity, for "real" experimental conditions of X-ray diffraction.

3.1. General case considerations, when there is a simultaneous vertical and horizontal divergence of an incident beam

An incident X-ray beam is usually affected simultaneously by both the vertical divergence and the horizontal divergence. Then the total intensity Io (λ) must

be written as an integral of the density of the distribution after γ and β, respectively:

$$I_0(\lambda) = \int_\gamma \int_\beta I_0(\gamma,\beta)\,d\gamma\,d\beta \qquad (10)$$

and I_0 (γ, β) represents the density of the incident intensity, ie it is a function of the divergence parameters!

Therefore, the pairs of angles (γ, β) will correspond to direction $\vec{u}_0$ (γ, β) which together with $\vec{H}(\gamma)$ gives the respective reference direction:

$$\vec{u}(\gamma,\vec{\beta}) = \vec{u}_0(\gamma,\beta) + \lambda\vec{H}(\gamma) \qquad (11)$$

Naturally, all vectors $\vec{s}$ that point to $\sum(\boldsymbol{\gamma},\boldsymbol{\beta})$ will contribute to the X-ray diffraction. Scanning after γ for a given β this is equivalent to estimating the contribution of the vertical divergence for β, ie Icv. Integration after β will represent the sum of all intensities of Icv (β). The integration interval after β will depend on the experimental geometry and, most importantly, will depend on the horizontal opening of the detector. However, Icv (β) may be limited by the vertical opening of the detector. The novelty of this approach is the consideration of the intensity distribution according to the divergence parameters (γ, β).

In the studied literature this aspect is reduced to silence because:

1) estimating I_0 (γ, β) is difficult to achieve,

2) if the specified aspects were taken into account, the theoretical treatment of the Lorentz factor would be very complicated.

In the simplifying hypothesis that I_0(γ, β) ≈ constant and that $|\boldsymbol{D_H}| << \mathbf{V_C}^*$ ($\mathbf{V_C}^*$ = the volume of the unit cell of the reciprocal space) it is admitted that the integral intensity diffracted by a crystallite is [6,13,14,15]**:**

$$I_H = I_0 \frac{g(H)\lambda^3}{\sin 2\theta}\frac{V}{V_C^2} = I_0 g(H) L(\theta)\frac{V}{V_C^2} \cong \frac{1}{\sin 2\theta}\cdot\frac{\lambda^3}{V_c^2}\cdot \delta V \qquad (12)$$

where: $L(\theta) = \frac{1}{\sin 2\theta}$ is Lorentz factor for a crystallite.

3.2. Estimation of the integral intensity given by a polycrystalline or powdery material

We will first address the case of a polycrystalline or powdery material made up of identical crystals. A polycrystalline material or a powdery material is a set of micronic crystallites that have average apparent diameters less than or equal to a few μm. The simplest case of polycrystalline aggregate is that in which the orientations of the crystallites are evenly distributed. In order to have an intuitive image of the orientations of the crystals, it will be considered that for a certain reflection ($h_1h_2h_3$)= $\vec{H}$ set of crystallites is equivalent to the $\vec{H}$ set of vectors associated with the orientation of each crystal. Thus, a collectivity of N identical crystals is equivalent to a distribution of N vectors $\vec{H}$ with solid angle 4π str.

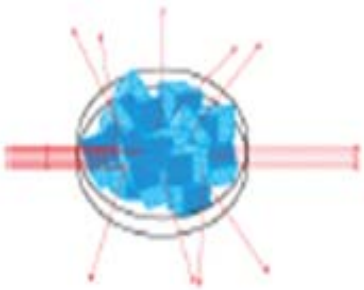


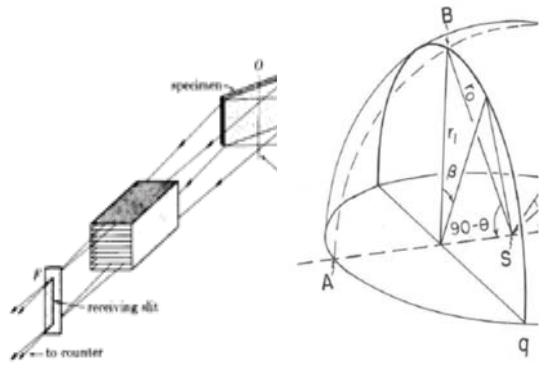
Figure 2. Schematic representation of beam diffraction by a powder sample

The distribution of $\vec{H}$ vectors is homogeneous if in any solid angle $d\Omega$ there is an equal number of $\vec{H}$ vectors regardless of its orientation. In this case the number of directions $\vec{H}$ in $d\Omega$ is

$$dN = \frac{N}{4\pi}d\Omega \qquad (13)$$

regardless of its orientation.

If one set of crystallites is irradiated with an appropriate X-ray to produce a diffraction phenomenon, then each crystallite will diffract independently of the other crystallites. Otherwise, the interfaces between the diffracted crystallite beams should also be taken into account, which would greatly complicate the estimation of the diffracted intensity of an ensemble of crystallites. In this context, the radiation received by the detector is the sum (integral) of the intensities diffracted by each crystallite, respectively the integral intensity of the whole, I_A is the sum of the integral intensities diffracted by each crystallite. In (figure 3) is presented the classical geometry of X-ray diffraction, by a polycrystalline sample in diffractometric assembly [16, 17].



a b

Figure 3. Diagram of the diffractometric assembly: a) the conventional Bragg-Brentano assembly; b) the theoretical model of Bragg-Brentano assembly diffraction [16-18]

The initial beam falls on sample S in the AD direction (figure 3b) and produces a principal diffraction maximum

at an angle of 2θ in the SC direction, where C is the center of the detector slot (figure 3a). The crystals that satisfy the diffraction condition have $\vec{H}$ vectors oriented at (90-θ) with respect to the incident beam, i.e. they form the generators of a cone that intersects the diffraction sphere (Ewald) forming the circle q, of radius $r_1=r_0\cos\theta$.

Each vector with the peak on the circle q (SB1) corresponds to a beam diffracted in the direction SC1, with C1 located on the circle p, of radius $r_2=r_0\sin 2\theta$. Crystallites that have $\vec{H}$ vectors with sufficiently small inclinations with respect to the circle q also produce diffracted waves, because the Ewald spheres associated with them of radius $r_0=1/\lambda$ intersect the reference node H. Consequently, the vectors that contribute to the formation of diffracted fascicles point in a hemispherical crown of length $2\pi r_1$ and width $2r_0\Delta\theta$, respectively delimit an area $4\pi r_0\cos\theta\Delta\theta$ (figure 4).

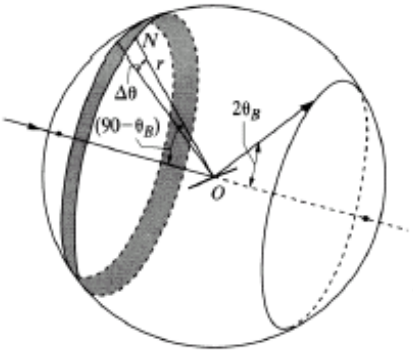


Figure 4. Schematic representation of the distributions of diffraction vectors in the case of a powder sample

This means that on the unit of length of the arc P will return a density of diffracted crystallites equal to:

$$n_2 = \frac{N4\pi r_0^2 \cdot \cos\theta\Delta\theta}{2\pi I_0 \cdot 2\pi r_0 \sin(2\theta)} = \frac{N\cos\theta\Delta\theta}{\pi\sin(2\theta)} = \frac{N}{2\pi r_0 \sin\theta} \quad (14)$$

If it is assumed that each crystal is completely immersed in the incident radiation and diffracts identically, then the integral intensity corresponding to the unit length of the arc P is:

$$I = \frac{1}{2\pi r_0 \sin\theta} \cdot I_0 \cdot g(H) \cdot \frac{\lambda^3}{V_C^2 \sin 2\theta} \cdot V = \frac{I_0 g(\vec{H})\lambda^3}{2\pi r_0 V_C^2} \cdot \frac{1}{\sin\theta \cdot \sin 2\theta} \cdot V \quad (15)$$

The term $\frac{1}{\sin\theta\cdot\sin 2\theta}$ which introduces the best correction for the expression of the integral intensity in the case of the powder method, is the Lorentz factor for the diffraction method on crystalline powders, respectively:

$$L = \frac{1}{\sin\theta \sin 2\theta} \quad (16)$$

In the literature, the above term, which expresses the Lorentz factor for the powder method, is described by the relation:

$$L = \frac{1}{4\sin\theta} \quad (17)$$

In the case of the diffractometric test, the detected intensity is proportional to the length of the arc P which intersects the detector slot (figure 3b, figure 5).

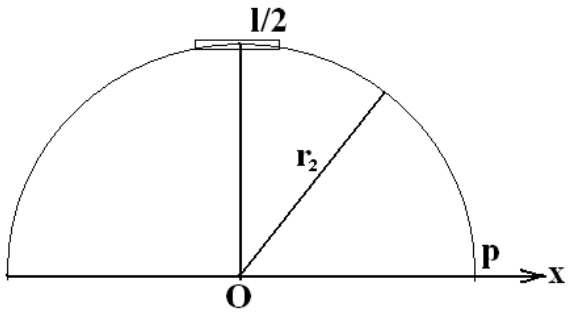


Figure 5. Schematic representation of diffraction geometry

The length of the spring contained in the slot in (Figure 5) is calculated with the relation:

$$\Delta p = 2\int_0^{\frac{e}{2}} \sqrt{1+\left[f(x)^{'}\right]^2} \cdot dx = 2 \cdot rq \arcsin\left(\frac{l}{2rq}\right) \quad (18)$$

where: $f(x) = \sqrt{r_0^2 - x^2}$.

Consequently, the intensity measured by the detector becomes:

$$I = 2\frac{I_0 g(H)\lambda^3}{2\pi r_0 V_C^2} \cdot V \cdot \frac{1}{\sin\theta \cdot \sin 2\theta} \cdot 2\arcsin\left(\frac{l}{2rq}\right) = \frac{I_0 g(H)\lambda^3 V}{\pi V_C^2 \sin\theta \sin 2\theta} \cdot \frac{r_2}{r_0} \arcsin\left(\frac{l}{2r_2}\right) \quad (19)$$

The length, height of the detector is of the order of 1 cm while r_0 is of the order of 3.5 cm. Be the most unfavorable, that is, for

$$\frac{l}{2r_2} = \frac{1}{2\cdot 2{,}5 \cdot \sin 2\theta} = \frac{0{,}02}{\sin 2\theta} .$$

For $2\theta\approx 5^{\circ}$, $\sin 15 = 0{,}2$ and $\frac{l}{2r_2} \cong 0{,}1$, i.e. $arcsin\left(\frac{l}{2r_2}\right) cu \frac{l}{2r_2}$ can be replaced without making a significant error.

In this context, the integral intensity measured by the detector is:

$$I_e \cong \frac{I_0 g(H)V}{2\pi V_C^2} \cdot \frac{\lambda^3}{\sin 2\theta \sin\theta} \cdot \left(\frac{l}{2r_0}\right) \quad (20)$$

4. DISCUSSIONS AND CONCLUSIONS

From the relation (20) respectively **I** (intensity) is directly proportional to the slit length and inversely proportional to r_0. Unfortunately, the experimental reality complicates things, i.e. if the width of the slot (w) is small or if the length of the slot is large, then the circle P may intersect the edges of the slot and not the ends, as shown in figure (figure 5). In this case, the detector introduces another proportionality factor. The calculation of intensity **I** for this case will be the subject of other studies that will be presented in future articles.

In conclusion, the diffraction geometry modifies the values of the integral diffraction intensities in the case of the powder method, with factors related to both the sample and the experimental factors. Thus, the operator must take into account the sizes l, w and whether or not the beam "bathe" the sample, in order to determine in the most real way what is the expression of the integral intensity for the assembly used.

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