THEORETICAL CONSIDERATIONS ON SOLUTION TO THE X-RAY PHASE PROBLEM USING MULTIPLE-BEAM DIFFRACTION

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1. Introduction

In every text-book about Crystallography one can read sentences like this: If the phases of the structure factors are known then the crystal structure is known, for one can compute the electron density $\rho(\mathbf{r})$ by a Fourier summation.

$$\rho(\mathbf{r}) = \frac{1}{\mathbf{V}} \sum_{\mathrm{h}} \mathbf{F}(\mathbf{h}) \exp - 2\pi \mathbf{i}\, \mathbf{r}\, \mathbf{h} \tag{1}$$

$$= \frac{1}{\mathbf{V}} \sum_{\mathrm{h}} |\mathbf{F}(\mathbf{h})| \exp \mathbf{i}\ \varphi(\mathbf{h}) \exp - 2\pi \mathbf{i}\, \mathbf{r}\, \mathbf{h}$$

However, the trouble is the lack of the detectors to be sensitive for phases, that means that only the moduli of the structure amplitudes $|\mathbf{F}(\mathbf{h})|$ can be derived from the measures intensities and its phases $\varphi(\mathbf{h})$ are unknown. These facts are called the phase problem of cristallography.

In order to get information on the phases of diffracted waves the only thing would be to carry out an interference experiment. For instance, superimposing two coherent waves with amplitudes $\mathbf{A}_1$ and $\mathbf{A}_2$ and phases α_1 and α_2 the resultant intensity $\mathbf{I}_{\mathbf{res}}$ depends on the amplitudes of the individual waves and on their phase-difference.

$$\mathbf{I}_{\mathrm{res}} \sim |\mathbf{A}_{\mathrm{res}}|^2 = |(\mathbf{A}_1 \exp \mathbf{i}\alpha_1 + \mathbf{A}_2 \exp \mathbf{i}\alpha_2)|^2 \tag{2}$$

$$= \mathbf{A}_1^{\,2} + \mathbf{A}_2^{\,2} + 2\, \mathbf{A}_1\, \mathbf{A}_2 \cos(\alpha_2 - \alpha_1)$$

This is the principle of interferometry and holography.

Interference of several coherent diffracted waves inside a crystal can be achieved with a so-called multiples-beam case. N-beam multiple diffraction occurs when N-1 sets of lattice planes are simultaneously brought into position to diffract the incident beam, i.e. N-1 sets of lattice planes simultaneously satisfy Bragg's diffraction condition. In other words N reciprocal lattice points, including the origin, are simultaneously on the surface of the Ewald sphere. Then all the diffracted wave fields interact with each other due to the fact that all the difference vectors of the reciprocal lattice $\mathbf{h}_i-\mathbf{h}_j$ of the excited Bragg waves terminate on the Ewald sphere. Interference effects change the intensity of each Bragg reflection. It is this intensity variation which gives the phase information.

Already in 1949 Lipscomb (1949) and at the same time Fankuchen have suggested to use the three-beam case for experimental phase determination. But no experimental results have been reported. At the end of the 70s and in the 80s the feasibility of this method has been shown by several authors (references can be found in the review article by Shih-Lin Chang (1987)).

For understanding the interaction among the diffracted waves inside the crystal, the dynamical theory for multiple x-ray diffraction must be used. For basic discussions we shall concentrate in this article on the three-beam case. We will give a brief survey of the dynamical theory for three-beam diffraction. The solution of the fundamental dynamical equations will be discussed with few mathematical and mostly physical arguments.

A systematically experimental way of generating multiple diffraction is an azimuthal scan, a so-called ψ-scan, around a scattering vector which is first aligned for reflection (primary reflection), i.e. it terminates on the Ewald sphere. By rotating the crystal in that way additional reciprocal lattice points can be brought on the Ewald sphere (secondary reflections). Thus multiple diffraction is generated. If exactly one additional secondary reflection is excited then a three-beam case is generated.

The experimental procedure is discussed in details in the lecture of E. Weckert.

2. Three-beam interference

This case is represented schematically in figure 1. Figure 1a shows the three-beam diffraction in crystal space, figure 1b in reciprocal space (Ewald construction). The indident beam is diffracted at the lattice plane denoted by the reciprocal lattice vector **h** and simultaneously at the lattice plane **g**. Thus, three strong waves are excited in the crystal: the incident wave and the two Bragg reflections **h** and **g**. If we look, for example, for the waves propagated in the direction of the **h**-reflection, denoted by **K**(**h**), then a superposition of two waves occurs: first, the directly diffracted wave at the lattice plane **h** and secondly, a so-called Umweg-wave, which is twice reflected at the lattice plane **g** and once more at the lattice plane **h–g** into the direction of the **h**– reflection. This lattice plane **h–g** must exist, since **h–g** is also a vector of the reciprocal lattice (see figure 1b). ±(**h–g**) couples the **h**– and the **g**–reflection. However, let us neglect for the moment that the **h**–reflection is also diffracted into the **g**–reflection by **g–h**. Generally speaking, the wave vectors of the three beams do not lie in one plane as it is drawn in figure 1 for the sake of simplicity.

Renninger (1937) has already proven experimentally that such an Umweg wave must exist. He observed the intensity of the forbidden (222)–

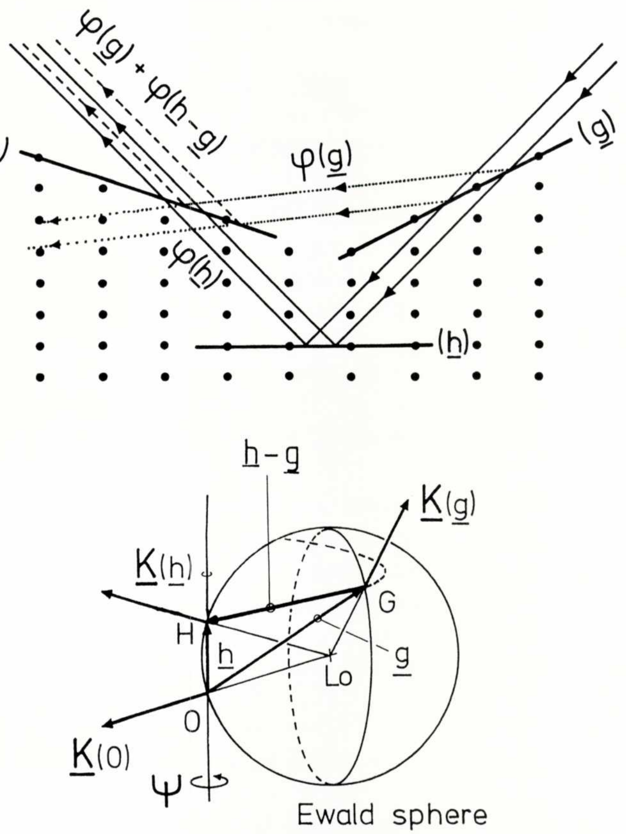


Fig. 1. Schematical representation of a three-beam case. a) in crystal space, b) in reciprocal space (Ewald construction).

reflection of diamond during a ψ-scan around (**222**). Each time when a second reciprocal lattice point passes the Ewald sphere a more or less strong diffracted intensity was measured, otherwise the intensity was very weak. Renninger called this effect Umweg-Anregung (Umweg excitation).

What is the phase difference between the primary reflection and the Umweg-reflection, which governs the resultant intensity due to interference (cf. eqn.(2)). The primary **h**-reflection has the phase $\varphi(\mathbf{h})$ due to the phase of its structure factor $\mathbf{F}(\mathbf{h})$. The Umweg-wave has the phase $\varphi(\mathbf{g}) + \varphi(\mathbf{h}-\mathbf{g})$ due to the structure factor product $\mathbf{F}(\mathbf{g})\mathbf{F}(\mathbf{h}-\mathbf{g})$ because it is twice diffracted at the corresponding lattice planes. Thus, the phase difference is given by:

$$\Phi_3(\mathbf{h}, \mathbf{g}) = \varphi(\mathbf{g}) + \varphi(\mathbf{h}-\mathbf{g}) - \varphi(\mathbf{h}) \tag{3a}$$

In the absence of anomalous dispersion effects (3a) can be rewritten:

$$\Phi_3(\mathbf{h}, \mathbf{g}) = \varphi(\mathbf{g}) + \varphi(\mathbf{h}-\mathbf{g}) + \varphi(-\mathbf{h}) \tag{3b}$$

$\Phi_3(\mathbf{h}, \mathbf{g})$ is a so-called triplet phase relationship.

As we shall see in the next chapter dynamical theory of multiple-beam diffraction gives an additional phase shift since in that regime Bragg reflection must be regarded as a spatial resonance phenomenon. Therefore, we must take a look at the dynamical theory for three-beam interference in order to understand the intensity variations during a ψ-scan through a three-beam diffraction position.

3. Three-beam dynamical theory

The fundamental equations of dynamical theory (5) are the solution of Maxwell's equations taking into account that the dielectric susceptibility has to be taken as translationally symmetric because of the short wavelength of x-rays in the order of atomic resolution. Thus, all the wavefields show also translational symmetry and they have to be expanded in Fourier (Bragg) sums over all reciprocal lattice vectors. For example, the dielectric displacement **D** is given by:

$$\mathbf{D}(\mathbf{r}) = \sum_{\mathbf{n}} \mathbf{D}(\mathbf{n}) \exp\{2\pi i \mathbf{K}(\mathbf{n})\} \quad \text{with} \quad \mathbf{K}(\mathbf{n}) = \mathbf{K} + \mathbf{n} \tag{4}$$

where **n** are the reciprocal lattice vectors.

Analogous sums must be taken for the magnetic and electric field.

Putting these sums into Maxwell's equations one gets the fundamental equations of dynamical theory (Pinsker, 1978):

$$\mathbf{D(n)} = \mathrm{R}(\mathbf{n}) \sum_{\mathbf{m} \neq \mathbf{n}} \chi(\mathbf{n} - \mathbf{m})\, \mathbf{D_n(m)}; \tag{5}$$

$\chi\,(\mathbf{n}) = \Gamma\,(\mathbf{F(n)}$; $\mathbf{n}$, $\mathbf{m}$ run over all the reciprocal lattice vectors.

D(n) denotes the dielectric displacement of the wavefield due to scattering vector **n.** $\mathbf{D_n(m)}$ stands for the projection of **D(m)** on **D(n)**, both are always perpendicular to their wave vector **K(n)** and **K(m),** respectively. **F(n)** is the structure factor. $\Gamma = (e^2/m_ec^2)\,(\lambda_0{}^2 / \pi V_c)$ (m_e: electron mass, V_c: volume of the unit cell) is a small number of the order of 10^{-7} and gives the strength of the coupling between **X**-ray and electrons in the framework of Thomson's scattering theory.

The physical content of (5) can be described as follows. Each wavefield **D(m)** scatters part of its amplitude into the wave field **D(n)** caused by the diffraction at the lattice plane **n–m**. The strength of the interaction between **D(m)** and **D(n)** is given by Γ**F(n–m)**. The resultant amplitude of the wave field **D(n)** is given by the interference of all contributions of the other wave fields **D(m)** to **D(n)**.

The excitation of the different wave fields **D(n)** is governed by the excitation error (Resonanzfehler)

$$\mathrm{R}(\mathbf{n}) = \mathrm{B}(\mathbf{n})^{-1} = \mathbf{K(n)}^2 / (\mathbf{K}^2 - \mathbf{K(n)}^2) \tag{6}$$

$$|\mathbf{K}| = \mathbf{s}_o(1 - \tfrac{1}{2}\,\Gamma\,\mathbf{F}(0)) = 1/\lambda; \quad \mathbf{s}_o = 1/\lambda_o$$

λ_o, λ are the wavelengths of vacuum and medium (crystal), respectively. That means, that only such wave fields are strongly excited and have to be taken into account, which fulfill Bragg's law. Then the length of the wave vector **K(n)** is equal to the radius of the Ewald sphere **K** and R(**n**) has its maximum value. R(**n**) decreases with the distance of the endpoint of **n** and **K(n)** from the Ewald sphere since **K(n)** = **K** + **n.**

This is the reason why it is allowed to cut off the infinite number of fundamental equations to three equations in a three-beam case, when only three strong waves **D(0)**, **D(h)** and **D(g)** are simultaneously excited.

To make things simpler, for the calculation of the amplitude of the primary reflection **D(h)**, we set all the scalar products, which take into account the projection $\mathbf{D_n(m)}$, equal to one. So we neglect the coupling between the π and σ polarization components of each wave field (Hümmer, Billy, 1986) and we are left with the following simplified system of equations for the three-beam case:

$$\begin{vmatrix} B(O) & \chi(-\mathbf{h}) & \chi(-\mathbf{g}) \\ \chi(\mathbf{h}) & B(\mathbf{h}) & \chi(\mathbf{h}-\mathbf{g}) \\ \chi(\mathbf{g}) & \chi(\mathbf{g}-\mathbf{h}) & B(\mathbf{g}) \end{vmatrix} \begin{vmatrix} \mathbf{D}(0) \\ \mathbf{D}(\mathbf{h}) \\ \mathbf{D}(\mathbf{g}) \end{vmatrix} = 0 \qquad (7)$$

To solve these equations for the ratio $\mathbf{D}(\mathbf{h})/\mathbf{D}(0)$ Bethe approximation is employed. This means the amplitude of $\mathbf{D}(\mathbf{g})$ is expressed in terms of $\mathbf{D}(0)$ and $\mathbf{D}(\mathbf{h})$ using the third equation of (7). Substituting in the second equation of (7), for instance, and solving for $\mathbf{D}(\mathbf{h})/\mathbf{D}(0)$ we get:

$$\mathbf{D}(\mathbf{h})/\mathbf{D}(0) = \mathrm{R}(\mathbf{h})\, \Gamma\, [\mathbf{F}(\mathbf{h}) + \Gamma\, \mathrm{R}(\mathbf{g})\, \mathbf{F}(\mathbf{g})\, \mathbf{F}(\mathbf{h}-\mathbf{g})] \qquad (8)$$

This result can be interpreted as follows. The amplitude in the two-beam case, i.e. no secondary reflections are excited, given by $\mathbf{D}_2(\mathbf{h})/\mathbf{D}(0) = \mathrm{R}(\mathbf{h})\, \Gamma\, \mathbf{F}(\mathbf{h})$ (first term of (8)) is modified by higher order terms due to excitation of other reflections. Obviously, if $\mathrm{R}(\mathbf{h})$ is negligibly small, i.e. Bragg's law for the **h**-reflection is not fulfilled, then no intensity can be observed in the direction of **K(h)**. This is also true, even though other wave fields are excited by carrying out a ψ-scan around **h**, so that other reciprocal-lattice points pass through the Ewald sphere. In this case Bragg's law for the scattering of the secondary **g**-reflection into the **h**-reflection is also not fulfilled, because the endpoints of the coupling vector **h–g** does not terminate on the Ewald sphere.

Thus, a strict prerequisite in order to observe the modification of the intensity of the **h**-reflection by the additional excitation of other reflection is to keep **h** precisely on the Ewald sphere during the ψ-scan.

In this case the primary **h**-reflection can be considered as a reference beam modulated by the secondary reflection. Thus the ψ-scan experiment generating multiple diffraction closely resembles holography. The interference contrast gives the phase information. Therefore, the amplitude (intensity) of the primary **h**-reflection is normalized and (8) is rewritten:

$$\mathbf{D}(\mathbf{h})/\mathbf{D}(0) = \mathrm{R}(\mathbf{h})\, \Gamma\, \mathbf{F}(\mathbf{h})\, [1 + \Gamma\, \mathrm{R}(\mathbf{g})\, \{\mathbf{F}(\mathbf{g})\, \mathbf{F}(\mathbf{h}-\mathbf{g})/\mathbf{F}(\mathbf{h})\}] \qquad (9)$$

Equs. (8) and (9) confirm the considerations of section 2. In the three beam case the wavefield **D(h)** is given by a superposition of two waves: the directly diffracted wave governed by the structure factor **F(h)** and the Umweg wave governed by the product of structure factors **F(g) F(h–g)**.

As can be seen from (9) (cf. the {term}) the phase relationship which governs the interference of both waves is given by equ. (3).

As can further be seen from (8) and (9) the resonance term (excitation error) R(**g**) governs the amplitude of the Umweg wave and causes an additional phase shift by 180° during the ψ-scan. We assume that it is carried out in such a way that the the endpoint of **g** passes the Ewald sphere from inside to outside. At the beginning of the ψ-scan when **g** terminates inside it is $|\mathbf{K}(\mathbf{g})|<|\mathbf{K}|$ since $\mathbf{K}(\mathbf{g}) = \mathbf{K} + \mathbf{g}$ (cf. Fig. 2), i.e. the denominator of R(**g**) is positive. When **g** approaches the Ewald sphere R(**g**) gets larger and

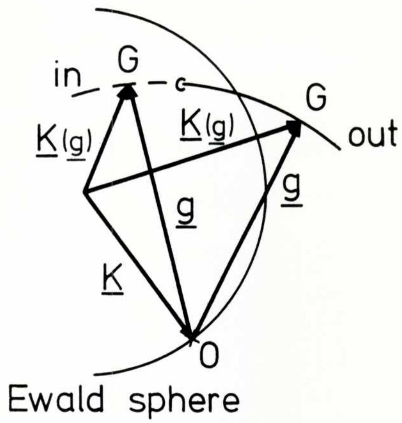


Fig. 2. Behaviour of **K(g)** during the ψ-scan from inside to outside.

larger since the denominator approaches to zero, i.e. the amplitude of the Umweg wave increases. It has its maximum value when **g** exactly lies on the Ewald sphere. When **g** leaves the Ewald sphere the amplitude of the Umweg wave decreases and R(**g**) has changed its sign, since $|\mathbf{K}(\mathbf{g})|>|\mathbf{K}|$ when **g** terminates outside (cf. figure 2). Changing its sign R(**g**) causes an additional phase shift by 180°. The behaviour of the amplitude and the phase shift of the Umweg wave during the ψ-scan is depicted in figures 3a and b.

Thus, the total phase relationship between the primary reflection and the Umweg reflection depends on ψ and is given by:

$$\Phi_{tot}(\psi) = \Phi_3 + \Delta(\psi) = \varphi(\mathbf{g}) + \varphi(\mathbf{h}-\mathbf{g}) - \varphi(\mathbf{h}) + \Delta(\psi) \qquad (10)$$

$$0 \leq \Delta(\psi) \leq 180^\circ \text{ for a } \psi\text{-rotation sense: inside} \rightarrow \text{outside}$$

That is all we need to discuss the three-beam ψ-scan profiles for different triplet phase relationships.

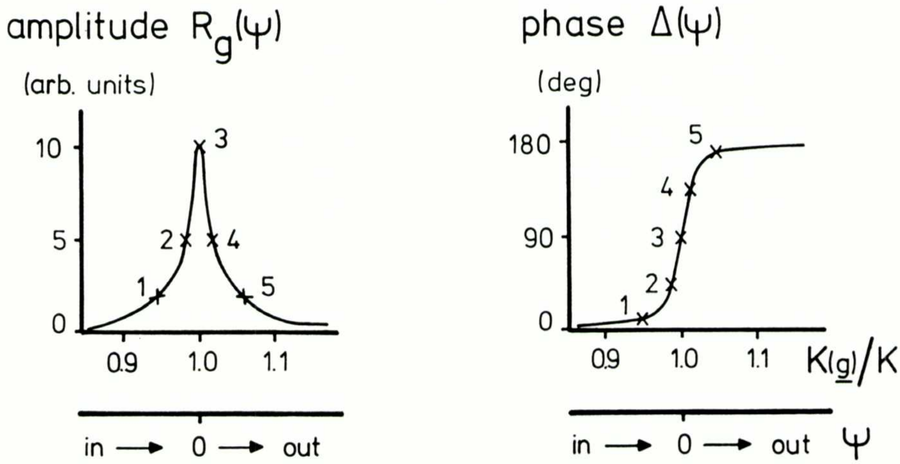


Fig. 3. Behaviour of the Umweg wave. a) amplitude, b) resonance phase shift

4. The Ψ-scan profiles

4.1. Ideal Profiles

As already discussed above, a basic requirement for multiple-beam ψ-scans is that the endpoint of the primary scattering vector **h** remains exactly on the surface of the Ewald sphere. Then the primary diffracted wave serves as a reference wave which amplitude remains constant. It is modulated by the Umweg waves due to the excitation of secondary reflections. This modulation gives information on the triplet phase relationship in case of three-beam diffraction.

As we shall see it is absolutely necessary to know the rotation sense of the ψ-scan experiment. To be clear we discuss the ψ-scan profiles in case of a rotation sense when the secondary scattering vector **g** passes the Ewald sphere from inside to outside. In the plots $\psi = 0$ gives the exact three-beam position: $\psi \leq 0$ means **g** terminates inside and $\psi \geq 0$ means **g** terminates outside.

Suppose the triplet phase of a three-beam case 0, **h**, **g** is zero: $\Phi_3 = 0°$. Then, at the beginning of the ψ-scan $\Delta(\psi) = 0$ and $\Phi_{tot} = 0$. The amplitude of the Umweg wave is very small and the two-beam intensity $|\mathbf{D}_2(\mathbf{h})|^2$ is observed. Scanning towards the three-beam position the amplitude of the Umweg wave incraeses and the primary wave and the Umweg wave interfere in a constructive way which leads to an increase of the resultant amplitude of **D(h)**. Thus, its intensity is increased. Very near to the three-beam position $\Delta(\psi)$ shifts very rapidly from 0 to 180°, then $\Phi_{tot} = 180°$.

That means the interference becomes destructive and the intensity is decreased. At the end of the ψ-scan when the amplitude of the Umweg wave gets smaller and smaller the two-beam intensity is observed again. This ψ-scan profile for $\Phi_3 = 0$ is shown in figure 4a.

For $\Phi_3 = 180°$ the ψ-scan profile is inversed with respect to $\psi = 0$ as shown in figure 4d. This behaviour is explained as follows. At the beginning of the ψ-scan the phase relationship between the interfering waves $\Phi_{tot} = \Phi_3 + \Delta(\psi) = 180 + 0 = 180°$. Thus, increasing the amplitude of the Umweg wave by scanning towards the three-beam position the intensity is first decreased because of destructive interference and then increased. Because, if **g** terminates outside the Ewald sphere then in that case $\Phi_{tot} = 180° + 180° = 0 \bmod 360°$, which leads to construcive interference.

It follows the explanation of the three-beam profiles for $\Phi_3 = +90°$ or $-90°$. In the case of $\Phi_3 = +90°$, Φ_{tot} shifts from 90° to 270° during the ψ-scan. At the exact the three-beam position $\Phi_{tot} = 90 + 90 = 180°$, since $\Delta(\psi) = 90°$ at $\psi = 0$ as can be seen in figure 3b and at the same time the amplitude of the Umweg wave has its maximum value. The result is a symmetrical profile around $\psi = 0$ caused by destructive interference. In the case of $\Phi_3 = -90°$, Φ_{tot} shifts from $-90°$ to $+90°$. Since at the exact three-beam position $\Phi_{tot} = -90° + 90° = 0$, a symmetrical profile is observed where the two-beam intensity is increased because of constructive interference. Both cases are depicted in figures 4b and c.

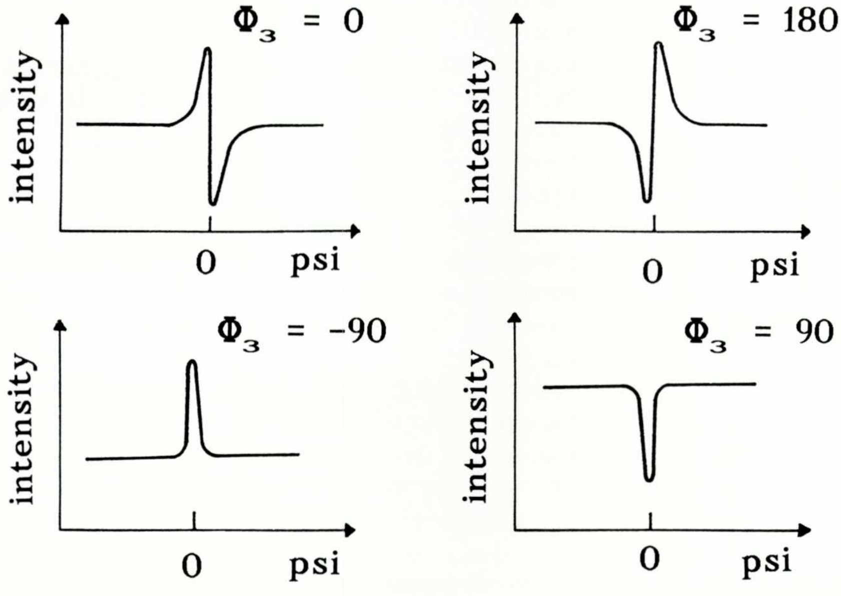


Fig. 4. Ideal three-beam diffraction profiles.

The three-beam diffraction ψ-scan profiles for triplet phases of + 45, + 135°, – 45 and – 135 must be betwen both the profiles of 0 and 90°, 90 and 180°, 0 and – 90°, – 90 and 180°, respectively. For example, the three-beam profile for + 45 must first show a slight increase (cos 45 > 0) and then a distinct decrease since in the exact three-beam position when $\Delta(\psi) = 90°$, so that $\Phi_{tot} = 135°$, and when the amplitude of the Umweg wave is highest, it results a destructive interference (cos 135 < 0). All the ideal ψ-scan profiles are depicted schematically in figure 6.

Hümmer & Billy (1986) explained the ideal ψ-scan profiles due to three-beam interference effects by means of phase-vector diagrams.

4.2. Profiles with Umweganregung und Aufhellung Effects

These ideal profiles can be only observed if the amplitudes of the interfering waves fulfill certain conditions. In general, the ψ-scan profiles consist of two parts: a phase-dependent part (ideal profile) due to the interference effect which bears the phase information and a symmetric phase-independent part due to the mean energy flow in a three-beam case which must be either incoherently added in case of Umweganregung effects or substracted in case of Aufhellung effects (Weckert & Hümmer, 1990).

Remember the fundamental equation of interference (2). The first two terms represent the incoherent addition of the intensities of each wave. The third term represents the interference effect. If, for example, $\mathbf{A}_1 \gg \mathbf{A}_2$ then the interference contrast is small compared to the phase independent intensity $\mathbf{A}_1^2 + \mathbf{A}_2^2$. A similar effect occurs if one of the **h**– or **g**–reflection is much more stronger or weaker then the other.

Suppose the **h**-reflection is very weak. This is similar to the original Renninger experiment (Renninger, 1937). Then, independent of the value of the triplet phase Φ_3 intensity of the **g**-reflection is coupled into the **h**-reflection via **h–g**. This would lead to strong Umweganregung effects which give no phase information like in the Renninger experiment. On the other hand, suppose the **h**-reflection is strong, then intensity is coupled out off the **h**-reflection via **g–h** into the **g**-reflection. This would lead to Aufhellung effects independent of the triplet phase. The ideal profiles can only be observed when the energy flow between the **h**-reflection and the **g**-reflection is well balanced, i.e. the same amount of energy is coupled out off and coupled into the **h**-reflection and **g**-reflection, respectively. This energy flow is governed by the law of conservation of energy. It can be described by a coupled system of differential equations (Moon & Shull, 1964). It depends only on the moduli of the structure factors involved in a three-beam case.

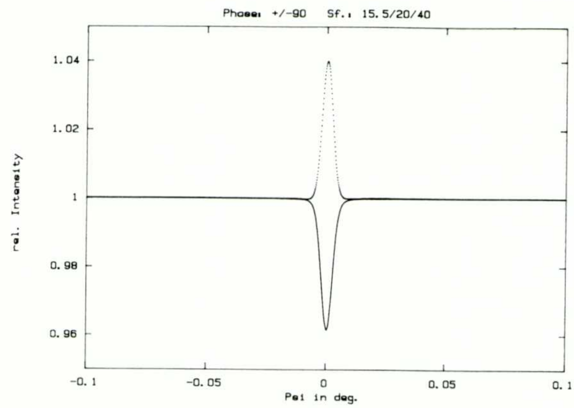
Existence of such Umweganregung and Aufhellung effects have been proved theoretically and experimentally by Weckert & Hümmer (1990) and Hümmer et. al. (1990). A theoretical example is shown in figure 5. The ψ-scan profiles are numerically calculated solving the fundamental equations of three-beam dynamical theory where the triplet phase involved is set to $\pm$ 90°. The criterion whether Umweganregung or Aufhellung occurs is the ratio $Q = |\mathbf{F(g)}\ \mathbf{F(h{-}g)}|/|\mathbf{F(h)}|^2$. Ideal profiles occur for $Q \approx 4$ (figure 5a). The profiles in figure 5b were calculated increasing $|\mathbf{F(g)}|$ from 20 to 75 leaving the other structure factor moduli constant, i.e. Q was increased to $\approx$ 13. As a result strong Umweganregung effects occur, so that the destructive interference effects in case of + 90° is overcompensated. But nevertheless, there is a big difference between both profiles. The relative intensity change of the two-beam intensity comes to + 28% for $\Phi_3 = -90$ and 6% for $\Phi_3 = +90$. That means that an interference effect of $\pm$ 11% is superimposed by an phase-independent Umweganregung of + 17%. The profiles in figure 5c were calculated decreasing $|\mathbf{F(g)}|$ to 5, i.e. $Q \approx 0.9$, leaving all the other parameters constant. As a result strong Aufhellung effects occurs coming to –7.5%, the interference effect being $\pm$ 1%. In the case that the Umweganregung or Aufhellung effects are dominating compared to the interference effect no phase information can be deduced.

Possible ψ-san profiles are listed in figure 6. The profiles with Umweganregung of Aufhellung effects are gained by adding a phase-independent symmetrcal Umweganregung or Aufhellung profile to the ideal ψ-scan profiles. In figure 6 the Umweganregung and Aufhellung intensity was chosen such that the destructive or constructive interference effects for triplet phases of + 90° and – 90° were just compensated.

The phase-independent part can be experimentally evaluated by comparing the ψ-san profiles of the two centrosymmetrically related three-beam cases **0/h/g** and **0/–h/–g** where for both cases the structure factor moduli remain constant, however their signs are reversed and therefore the sign of the triplet phase involved is also reversed.

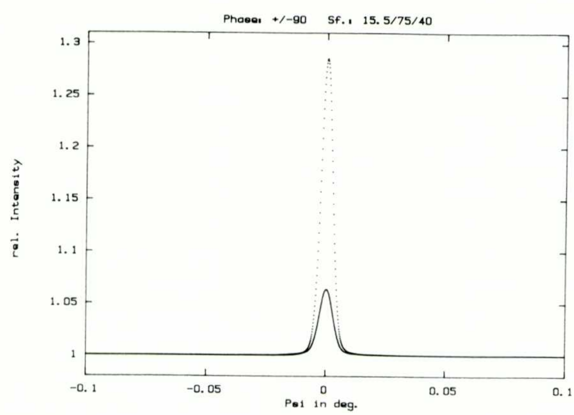
It can be seen that in these cases phase determination is possible with an accuracy of about 45° since all the ψ-scan profiles show significant differences. Moreover, also the sign of the triplet phases of non-centrosymmetric structures can be determined. This is extremely important for solving the enantiomorphy problem in light atom structures where anomalous dispersion effects are very weak. By determination of the sign of a triplet phase the absolute configuration is absolutely fixed. It should be pointed out that for the three-beam method no anomalous dispersion effects are needed.

a)



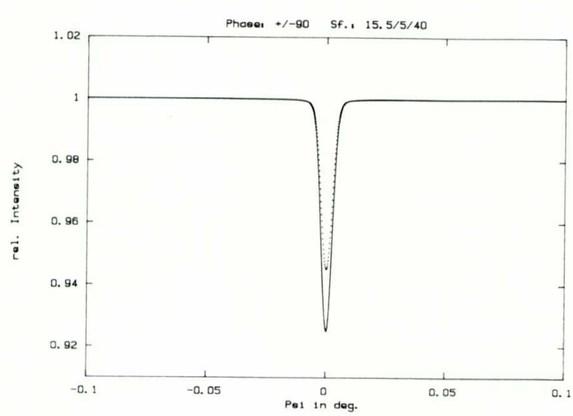
|**F(h)**| = 15,5;
|**F(g)**| = 20;
|**F(h–g)**| = 40

b)



|**F(h)**| = 15,5;
|**F(g)**| = 75;
|**F(h–g)**| = 40

c)



|**F(h)**| = 15,5;
|**F(g)**| = 5;
|**F(h–g)**| = 40

Fig. 5. Influence of the structure factor moduli on Umweganregung and Aufhellung, calculations by dynamical theory; solid: $\Phi_3 = +90$, dotted: $\Phi_3 = -90$.

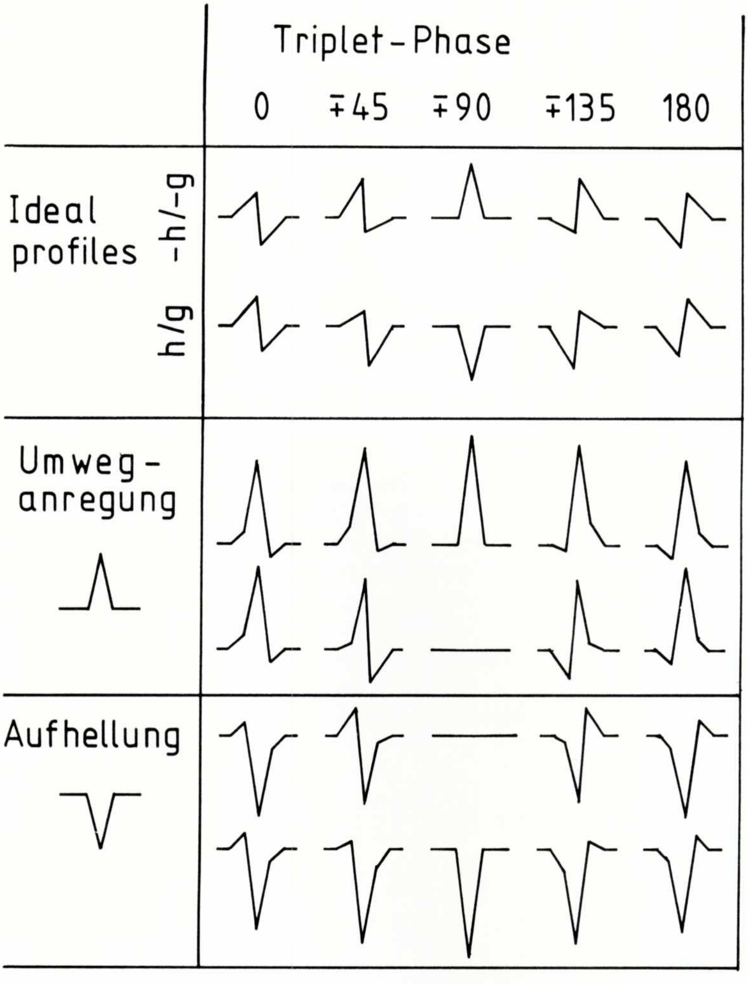


Fig. 6. Catalogue of possible ψ-scan profiles in case of three-beam diffraction.

5. SUMMARY

It has been shown that in case of three-beam diffraction an interference of two wave fields occur: the directly diffracted primary wave and the 'Renninger' Umweg wave are propagated in the same direction. Their phase difference is a triplet phase relationship which gives rise to significant ψ-scan profiles. In general, each ψ-scan profile is a superposition of a phase-dependent interference profiles and phase-independent Umweganregung of Aufhellung profile. By comparing the ψ-scan profiles of the two centrosymmetrical related three-beam cases **0/h/g** and **0/–h/–g** these latter part can be evaluated and experimental determination of the triplet phase is possible with an accuracy of about 45°. Since also the sign of the triplet phase can be determined the absolute structure in case of non-centrosymmetry can be fixed.

ABSTRACT

It is shown that in case of three-beam difraction an interference of two wave fields occur: the directly primary wave diffracted at the lattice plane of **h** and the 'Renninger' Umweg wave successively diffracted at the lattice plane of **g** and **h–g**, both are propagated in the same direction. Their total phase difference is given by a triplet phase relationship of the structure factor ratio F(**g**) F(**g–g**)/F(**h**) and an additional resonance phase shift by 180° in case of an azimuthal scan around the primary scattering vector **h**(ψ-scan) through a three beam position **0/h/g**. This total phase difference leads to significant ψ-scan profiles for each triplet phase. In general, each ψ-scan profile is a superposition of a phase-dependent interference profile and phase-independent Umweganregung or Aufhellung profile which depends on the structure factor moduli. By comparing the ψ-scan profiles of the two centrosymmetrical related three-beam cases 0/**h**/**g** and 0/–**h**/–**g** these latter pats can be evaluated and experimental determination of the triplet phase is possible with an accuracy of about 45°. Moreover, in case of non-centrosymmetry the sign of the triplet phase can be determined. Thus, the absolute structure can be fixed.

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