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Direct Phase Determination from Resonant γ-Quantum Diffraction Experiments

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The problem of phase determination from experiments on the Bragg reflexion of γ-quanta in nuclear and electronic Rayleigh scattering is considered. In the general case of diffraction, the solution of the integral equation is obtained which connects the experimental reflecting power $R_h^{(i)}(v)$ with the diffracted integral (over angles) intensity $R_h(u)$ (v is the velocity of the Mössbauer source with respect to a scatterer, u is the energy deviation parameter from the exact resonance energy of the Mössbauer nuclei). The expressions for the magnitude and sign of the phase of the electronic structure factor are derived in the cases of perfect and mosaic crystals. The phase is determined from the asymptotic behaviour and the square of the experimental curve $R_h^{(i)}(v)$.

1. Introduction

Up to now, in X-ray diffraction analysis, different direct and indirect methods (Carpenter, 1969; Ramachandran & Srinivasan, 1970) have been developed, which permit a reliable enough interpretation of the atomic structure of crystals and molecular complexes from the angular distribution and the intensity of X-rays scattered. These methods, based on the use of a set of electronic structure factors $|F_{\mathbf{h}}^{(e)}| \exp (i\varphi_{\mathbf{h}}^{(e)})$ ($|F_{\mathbf{h}}^{(e)}|$ and $\varphi_{\mathbf{h}}^{(e)}$ are the amplitude and phase respectively) for the calculation of the electron-density distribution are continually being improved.

However, owing to the discovery of the Mössbauer effect (Mössbauer, 1958, 1959), there appeared a new possibility of phase determination from resonant γ-quantum diffraction experiments (Raghaven, 1961; Moon, 1961; Zhdanov & Kuz'min, 1968). The interference of the channels of the resonance nuclear and electronic Rayleigh scattering was experimentally confirmed by a number of authors (Black, Evans & O'Connor, 1962; Black, Longworth & O'Connor, 1964; O'Connor & Black, 1964; Voitovskii, Korsunskii, Novikov & Pazkin, 1968). The consequent theory of Bragg diffraction of the resonant γ-quanta was given by Kagan, Afanas'ev & Perstnev (1968). In two papers by Mössbauer and co-workers (Parak, Mössbauer & Hoppe, 1970; Parak, Mössbauer, Biebl, Formanek & Hoppe, 1971) a special analysis was performed to determine the phases for protein and potassium ferricyanide $K_3Fe(CN)_6$. In particular, by Parak *et al.* (1971), the interference curves were computed by varying the phase parameter $\varphi_{\mathbf{h}}^{(e)}$ for reflexions $\mathbf{h}=020$ and 040 of the crystal $K_3Fe(CN)_6$. Further, by comparison of the numerically calculated and experimental curves the phases $\varphi_{020}^{(e)}$, $\varphi_{040}^{(e)}$ were determined.

The purpose of the present paper is to discuss a new approach to direct phase determination from γ-spectroscopy diffraction experiments.

2. Theory

Consider a γ-quantum beam falling on the surface of a crystal. Of this beam, the fraction f_s (f_s is the Mössbauer factor of the source) of all γ-quanta undergoes interference nuclear–electronic scattering and the fraction $(1-f_s)$ purely electronic scattering. Let us introduce the energy distribution function $I_s(E,v)$ of the γ-quanta emerging from a source. The function $I_s(E,v)$ (v being the source velocity with respect to the scatterer) satisfies the normalization condition

$$\int_{-\infty}^{\infty} \mathrm{d}E I_s(E,v)=1 \, .$$

When the total intensity of the resonant γ quanta diffracted along the **h** direction with a given energy is $R_{\mathbf{h}}(E)$, the integral reflecting power will be equal to

$$R_{\mathbf{h}}^{(i)}(v)=f_s\int_{-\infty}^{\infty} \mathrm{d}E I_s(E,v) R_{\mathbf{h}}(E)+(1-f_s)R_h(\infty) \, . \qquad (1)$$

The integral relation (1) is basic for determination of the phase which enters only the expression $R_{\mathbf{h}}(E)$ as a parameter. When E goes to infinity, the nuclear resonant scattering is practically negligible and $R_{\mathbf{h}}(E)$ is determined by the purely electronic scattering. This means that $R_{\mathbf{h}}(\infty)$ contains no information about the phase $\varphi_{\mathbf{h}}^{(e)}$.

The explicit expression for $R_{\mathbf{h}}(E)$ essentially depends on the degree of crystal perfection, the collimation of the incident beam and the diffraction geometry (the Bragg or Laue diffraction cases). The formula for the intensity $R_{\mathbf{h}}(E)$ in the case of Bragg diffraction was given by Afanas'ev & Perstnev (1969).

In order to emphasize the essence of a new approach to phase determination we further restrict our treatment to Bragg diffraction on thick crystals, when the crystal thickness is much greater than the γ-quantum absorption length. In this case the analysis of the problem is simplified. From the treatment below it will be seen that the method developed in the present paper does not depend on the above assumption and solves the phase problem in the general case of resonant γ-quantum diffraction.

To describe the energy distribution of the incident γ-quanta one uses the Lorentz function

$$I_s(E,v)=\frac{1}{\pi}\,\frac{\Gamma_s/2}{\left[E-E_s\left(1+\frac{v}{c}\right)\right]^2+(\Gamma_s/2)^2}\,. \qquad (2)$$

Here E_s, Γ_s are the mean energy and the width of the Mössbauer line of the source, c is the velocity of light. The expression (2) for $I_s(E,v)$ is practically exact under the condition that the Mössbauer line is not split and that the self-absorption of the γ-quanta inside the source is negligible.

Let us introduce the following notation

$$\gamma=\frac{\Gamma_s}{\Gamma_c}\,,\; u=\frac{E_s\left(1+\frac{v}{c}\right)-E_c}{\Gamma_c/2}\,,\; u'=\frac{E-E_c}{\Gamma_c/2}\,, \qquad (3)$$

where E_c and Γ_c are the energy and width of the Mössbauer resonance level of the crystal nuclei. E_c and Γ_c are, in general, different from E_s and Γ_s. We assume for simplicity that all resonant nuclei are identical.

Using equation (3) one can transform (1) and (2) to the form

$$R^{(i)}_{\mathbf{h}}(u)-R_{\mathbf{h}}(\infty)=f_s\int_{-\infty}^{\infty}\mathrm{d}u'I_s(u-u')[R_{\mathbf{h}}(u')-R_{\mathbf{h}}(\infty)], \qquad (4)$$

$$I_s(u-u')=\frac{1}{\pi}\,\frac{\gamma}{(u-u')^2+\gamma^2}\,. \qquad (5)$$

The relation (4) can be considered as the integral equation for finding the function $R_{\mathbf{h}}(u)$ *via* the experimental reflecting power $R^{(i)}_{\mathbf{h}}(u)$. Making the direct and inverse Fourier transformations of equation (4) one after the other and taking account of equation (5) one obtains

$$f_s[R_{\mathbf{h}}(u)-R_{\mathbf{h}}(\infty)]=\cos\left(\gamma\frac{\partial}{\partial u}\right)[R^{(i)}_{\mathbf{h}}(u)-R_{\mathbf{h}}(\infty)]$$
$$+\frac{1}{\pi}\sin\left(\gamma\frac{\partial}{\partial u}\right)\text{v.p.}\int_{-\infty}^{\infty}\mathrm{d}u'\,\frac{R^{(i)}_{\mathbf{h}}(u')-R_{\mathbf{h}}(\infty)}{u-u'}\,. \qquad (6)$$

Here $\genfrac{}{}{0pt}{}{\sin}{\cos}\left(\gamma\frac{\partial}{\partial u}\right)$ is the symbol for the corresponding trigonometric series in powers of the differential operator $\gamma\partial/\partial u$.

Bearing in mind that $R^{(i)}_{\mathbf{h}}(u)$ is the experimental function, it is clear that the practical use of equation (6) is rather problematic. However, from equation (6) one can obtain asymptotic relations, which, in principle, permit a simple determination of the phase $\varphi^{(e)}_{\mathbf{h}}$. Indeed, when the variable u is large the integral intensity $R_n(u)$ may be shown to behave as follows

$$R_{\mathbf{h}}(u)=R_{\mathbf{h}}(\infty)+\frac{A}{u}+\frac{B}{u^2}+\mathrm{O}\left(\frac{1}{u^3}\right)\,. \qquad (7)$$

The coefficients A and B are functions of the phase parameter $\varphi^{(e)}_{\mathbf{h}}$.

After taking equations (6) and (7) into account, one readily obtains for the coefficients A and B

$$A=\frac{1}{f_s}\lim_{u\to\infty}u[R^{(i)}_{\mathbf{h}}(u)-R_{\mathbf{h}}(\infty)]\,, \qquad (8)$$

$$B=\frac{1}{f_s}\lim_{u\to\infty}u^2\left[R^{(i)}_{\mathbf{h}}(u)-R_{\mathbf{h}}(\infty)-\frac{A}{u}\right]-\frac{\gamma}{\pi f_s}$$
$$\text{v.p.}\int_{-\infty}^{\infty}\mathrm{d}u'[R^{(i)}_{\mathbf{h}}(u')-R_{\mathbf{h}}(\infty)]\,. \qquad (9)$$

Therefore the problem of phase determination may in practice be reduced to finding two real parameters, A and B, which are determined from the asymptotic behaviour and the square of the experimental interference curve in accordance with equations (8) and (9). If the coefficients A and B of the expansion (7) are known from experiment, one can easily derive the equations for the phase of the electronic structure factor.

Consider, for example, γ-quantum Bragg diffraction by perfect and mosaic crystals when the splitting of the Mössbauer resonance level is negligible. As was mentioned, the proper expressions for $R_{\mathbf{h}}(u)$ were obtained for the case of the Bragg diffraction (b is the asymmetry parameter, $b<0$) by Afanas'ev & Perstnev (1969)

$$R_{\mathbf{h}}(u)=\frac{8}{3\sin 2\theta_B}\overline{|\chi_{\mathbf{h}0}|\sqrt{\left|\frac{\chi_{\mathbf{h}0}}{b\chi_{0\mathbf{h}}}\right|}P(s,q)}\,,$$

$$s=\frac{\mathrm{Im}\,\chi_{00}+|b|\,\mathrm{Im}\,\chi_{\mathbf{hh}}}{2\sqrt{|b|\,|\chi_{0\mathbf{h}}\chi_{\mathbf{h}0}|}}\,,\; q=\frac{2\sqrt{|b|}\,|\mathrm{Im}\sqrt{\chi_{0\mathbf{h}}\chi_{\mathbf{h}0}}|}{\mathrm{Im}\,\chi_{00}+|b|\,\mathrm{Im}\,\chi_{\mathbf{hh}}} \qquad (10)$$

[*cf.* Afanas'ev & Perstnev (1969) for details and the explicit form of the function $P(s,q)$].

In the case of a mosaic crystal the function $R_{\mathbf{h}}(u)$ under the usual experimental conditions is given by

$$R_{\mathbf{h}}(u)=\frac{\pi\Delta\theta}{2\delta\sin 2\theta_B}\,\frac{\overline{|\chi_{\mathbf{h}0}|^2}}{\mathrm{Im}\,\chi_{00}+|b|\,\mathrm{Im}\,\chi_{\mathbf{hh}}}\,. \qquad (11)$$

Equation (11) is derived under the assumptions that the secondary extinction is negligible and the angle collimation of the incident beam $\Delta\theta$ is less than the characteristic mosaic misorientation δ. When $\Delta\theta>\delta$ one has to put the factor $\Delta\theta/\delta$ in equation (11) equal to unity (mosaic blocks are assumed to be uniformly disordered over the angle δ).

In equation (10) and (11) the bar above denotes an average over the incident γ-quantum polarizations. With no nuclear level splitting the dynamical coefficients χ_{00}, $\chi_{0\mathbf{h}}$, $\chi_{\mathbf{h}0}$, $\chi_{\mathbf{hh}}$ take the form

$$\chi_{00}=\chi^{(e)}_0+\frac{\chi^{(n)}_{00}}{u+i}\,,\; \chi_{\mathbf{h}0}=\chi^{(e)}_{\mathbf{h}}C^{(e)}+\frac{\chi^{(n)}_{\mathbf{h}0}C^{(n)}}{u+i}\,,$$
$$\chi_{0\mathbf{h}}=\chi^{(e)}_{-\mathbf{h}}C^{(e)}+\frac{\chi^{(n)}_{0\mathbf{h}}C^{(n)}}{u+i}\,,\; \chi_{\mathbf{hh}}=\chi^{(e)}_0+\frac{\chi^{(n)}_{\mathbf{hh}}}{u+i}\,, \qquad (12)$$

where the upper indices e and n correspond to Fourier components of the electronic and nuclear polarizability. In the formulae (12) the resonance dependence of the nuclear components is explicitly distinguished. The electronic component of the polarizability $\chi_{\mathbf{h}}^{(e)}$ is connected with the electronic structure factor by the usual relation

$$\chi_{\mathbf{h}}^{(e)} = -\frac{\lambda^2}{\pi V_0}\frac{e^2}{mc^2}F_{\mathbf{h}}^{(e)}$$

(V_0 being the unit cell volume).

3. Phase determination

Writing the coefficients $\chi_{\mathbf{h}}^{(e)}$ and $\chi_{\mathbf{h}0}^{(n)}$ as follows

$$\chi_{\mathbf{h}}^{(e)} = -|\chi_{\mathbf{h}}^{(e)}| \exp(i\varphi_{\mathbf{h}}^{(e)}) , \quad \chi_{\mathbf{h}0}^{(n)} = -|\chi_{\mathbf{h}0}^{(n)}| \exp(i\varphi_{\mathbf{h}}^{(n)})$$

and neglecting the dispersion corrections in the definition of the electronic phase $\varphi_{\mathbf{h}}^{(e)}$, one finds the following equations for $\varphi_{\mathbf{h}}^{(e)}$ (the nuclear phase $\varphi_{\mathbf{h}}^{(n)}$ is assumed to be known):

(*a*) for a perfect crystal, when $|u| \gg \max(1, |\chi_{\mathbf{h}0}^{(n)}/\chi_{\mathbf{h}}^{(e)}|)$ the function $P(s,q)$ in equation (10) is approximately equal to $1-3\pi s/4$ and using the relations (7), (10) and (12) one obtains, after a number of simple transformations

$$\frac{A}{\bar{R}_{\mathbf{h}}(\infty)} = \left(\frac{\overline{C^{(n)}C^{(e)}}}{|C^{(e)}|}\right) \times \frac{|\chi_{\mathbf{h}0}^{(n)}| \cos\varphi_{\mathbf{h}}}{|\chi_{\mathbf{h}}^{(e)}|(1+|\cos 2\theta_B|)/2 - 3\pi\mu_e/8\sqrt{|b|}}$$

$$\frac{B}{\bar{R}_{\mathbf{h}}(\infty)} = \frac{\dfrac{\overline{(C^{(n)})^2}}{|C^{(e)}|}\dfrac{|\chi_{\mathbf{h}0}^{(n)}|^2}{2|\chi_{\mathbf{h}}^{(e)}|}\sin^2\varphi_{\mathbf{h}} - \dfrac{\overline{C^{(n)}C^{(e)}}}{|C^{(e)}|}|\chi_{\mathbf{h}0}^{(n)}| \sin\varphi_{\mathbf{h}} - 3\pi\mu_n/8\sqrt{|b|}}{|\chi_{\mathbf{h}}^{(e)}|(1+|\cos 2\theta_B|)/2 - 3\pi\mu_e/8\sqrt{|b|}} \qquad (13)$$

(*b*) for a mosaic crystal when $|u| \gg \max(1, \sqrt{\mu_n/\mu_e})$ one has [*cf.* equations (7), (11), (12)]

$$\frac{A}{\bar{R}_{\mathbf{h}}(\infty)} = 2\frac{|\chi_{\mathbf{h}0}^{(n)}|}{|\chi_{\mathbf{h}}^{(e)}|}\cos\varphi_{\mathbf{h}}\frac{\overline{2C^{(e)}C^{(n)}}}{1+\cos^2 2\theta_B}, \qquad (14)$$

$$\frac{B}{\bar{R}_{\mathbf{h}}(\infty)} = \frac{|\chi_{\mathbf{h}0}^{(n)}|^2\,\overline{(C^{(n)})^2} - 2|\chi_{\mathbf{h}}^{(e)}||\chi_{\mathbf{h}0}^{(n)}| \sin\varphi_{\mathbf{h}}\,\overline{C^{(e)}C^{(n)}}}{|\chi_{\mathbf{h}}^{(e)}|^2(1+\cos^2 2\theta_B)/2} - \frac{\mu_n}{\mu_e}.$$

In equations (13) and (14) one puts $\varphi_{\mathbf{h}} = \varphi_{\mathbf{h}}^{(e)} - \varphi_{\mathbf{h}}^{(n)}$, $\mu_n = \chi_{00}^{(n)} + |b|\chi_{\mathbf{hh}}^{(n)}$, $\mu_e = (1+|b|) \operatorname{Im} \chi_0^{(e)}$.

It should be noted that in the case of a mosaic crystal the simple equation for the phase $\varphi_{\mathbf{h}}^{(e)}$ may be derived not only in the region of the asymptotic behaviour of $R_{\mathbf{h}}(u)$. From this, the function $R_{\mathbf{h}}(u)$ is equal to

$$R_{\mathbf{h}}(u) = R_{\mathbf{h}}(\infty) + \frac{Au+B}{u^2+1+\mu_n/\mu_e}. \qquad (15)$$

Now inserting equation (15) into the basic equation (4) and taking equation (5) into account, the integration over u' in (4) may be carried out exactly. As a result, one obtains the final expression for the integral reflecting power

$$R_{\mathbf{h}}^{(i)}(u) = R_{\mathbf{h}}(\infty) + \frac{Au + B(\gamma+\sqrt{1+\mu_n/\mu_e})\,/\,\sqrt{1+\mu_n/\mu_e}}{u^2+(\gamma+\sqrt{1+\mu_n/\mu_e})^2}.$$

Thus, in this particular case a phase-determination method different from (14) exists in principle, when the experimental function $R_{\mathbf{h}}^{(i)}(u)$ may be used for arbitrary values of the variable u.

The formulae (13) and (14) are obtained under the simple assumption that all the nuclei inside a unit cell are equivalent. Further, the dispersion corrections are not taken into account in the definition of the electronic structure phase.

In analysing the physical situation, it may be necessary to consider such factors as the dispersion corrections, the quadrupole or magnetic splitting of the Mössbauer nuclear level and the non-equivalence of the Mössbauer nuclear positions inside a unit cell. Nevertheless, it is clear that the general character of the relations (13), (14) will remain unchanged. This means that phase determination from the resonant γ-quantum diffraction experiments should be possible.

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