X-ray Reflection Curves of Crystals with Randomly Distributed Microdefects in the Bragg Case

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Abstract

The formalism of the optical coherence has been applied to the description of the Bragg-case dynamical X-ray diffraction from crystals with randomly distributed amorphous spheres. Explicit formulas have been found for the reflection curves of such crystals in the first and second approximations of the iterative solution of the Takagi equations. It is shown that if the coherent plane wave falls on the crystal the diffracted wave consists of two parts – the plane coherent wave (which corresponds to the diffraction from a perfect crystal with a modified value of the Debye–Waller factor) and the partially coherent wave (diffusion scattering). The form of the partially coherent contribution to the reflection curve is discussed and its dependence on the defect diameter and the defect concentration. From the curves the integrated intensities are obtained. It is proved that the integrated intensity of the waves diffracted from such crystals depends linearly on the relative disturbed volume of the crystal and in the first approximation it does not depend on the defect diameter if this volume remains constant.

1. Introduction

X-ray diffraction from crystals with randomly distributed microdefects is described usually on the basis of kinematical diffusion scattering of X-rays. In previous papers (Holý, 1980, 1982*a,b,c*), the dynamical diffraction of X-rays was described by means of the formalism of optical coherence. It was shown within the framework of the dynamical diffraction theory that the correlated displacements of the atoms in the crystal cause the decrease in the degree of coherence of the diffracted wave and thus the shape of the reflection curve and the angular distribution of the diffracted intensity (diffusion scattering) are changed. The general principles formulated by Holý (1982*a*) were applied (Holý, 1982*b*) for the computation of Laue-case reflection curves and it was proved that the

kinematical limit of the curves obtained is equal to that computed by the usual formalism of diffusion scattering (Dederichs, 1971; Krivoglaz, 1967).

The aim of this paper is to apply the general results for Bragg-case diffraction from crystals with small amorphous spherical volumes randomly distributed over the crystal volume. We obtain the explicit formulas for reflection curves of such crystals and we compute the integrated intensities of the diffracted wave.

2. General theory

The theoretical description of the dynamical diffraction from crystals with randomly distributed defects was based on the iterative solution of the Takagi equations in the integral form which was formulated by Afanas'ev & Kohn (1971). The details of the computation as well as the meaning of the symbols used are given in the paper by Holý (1982*a*) – referred to as I.

The mutual coherence function (MCF) $\hat{\Gamma}(r,r')$ of the waves emitted from a disturbed crystal, which is defined as

$$\hat{\Gamma}(r,r') = \langle\langle \mathbf{D}(r) \otimes \mathbf{D}^+(r') \rangle_E \rangle_T, \qquad (1)$$

can be written in a first approximation in the following form [*cf.* I, equation (39)]:

$$\hat{\Gamma}^{(1)}(r_a,r'_a) = \hat{\Gamma}^{(0)}(r_a,r'_a) + \exp[2\pi i(\Delta . r_a - \Delta^* . r'_a)]$$

$$\times \int_V \int_V dr\,dr'\, \hat{G}(r_a - r)$$

$$\times \langle \hat{p}(r)\, \hat{\gamma}^{(0)}(r,r')\, \hat{p}^+(r') \rangle_E \, \hat{G}^+(r'_a - r'), \qquad (2)$$

$\hat{\gamma}^{(0)}(r,r')$ is the MCF of the waves in the perfect crystal with the Debye–Waller factor $\langle \exp[-2\pi i\mathbf{h} . \mathbf{u}(r)] \rangle_E$ ('quasiperfect crystal'), $\hat{\Gamma}^{(0)}(r_a,r'_a)$ is the MCF of the waves emitted from the quasiperfect crystal.

In this paper we are concerned with the Bragg case of diffraction. Then

$$\gamma^{(0)}_{ij}(r,r') = I_{ij} \exp[-2\pi i(\kappa . r - \kappa^* . r')], \quad i,j = 0, h, \quad (3)$$

if the plane coherent wave falls on the crystal. κ is the physically correct solution of the dispersion relation (I.43) for the given direction of the incident rays. For the coefficients I_{ij}

$$\hat{I} = \{I_{ij}\} = I_e \left\| \begin{matrix} 1 & c^* \\ c & cc^* \end{matrix} \right\| \tag{4}$$

holds, where I_e is the intensity of the primary beam, c is the complex reflectivity of the quasiperfect crystal. Green's function of the quasiperfect crystal equals that of the perfect crystal with the changed value of χ_h. Then in the Bragg case (cf. Afanas'ev & Kohn, 1971)

$$\hat{G}(r - r') = \frac{\delta(y - y')}{\sin 2\theta}$$

$$\times \left\| \begin{matrix} \delta(s_h - s'_h)\,\Theta(s_0 - s'_0) & 0 \\ & \\ i\pi K \chi'_h R(r - r') & \dfrac{\partial R(r - r')}{\partial s'_0} \end{matrix} \right\| \tag{5}$$

holds, where

$$R(r - r') = \Theta(s_0 - s'_0)\,\Theta(s_h - s'_h)\Bigg(J_0\{2\pi K(\chi'_h \chi'_{-h})^{1/2}$$

$$\times [(s_0 - s'_0)(s_h - s'_h)]^{1/2}\}$$

$$- \frac{\gamma_0}{\gamma_h} \frac{s_0 - s'_0}{s_h - s'_h} J_2\{2\pi K(\chi'_h \chi'_{-h})^{1/2}$$

$$\times [(s_0 - s'_0)(s_h - s'_h)]^{1/2}\} \Bigg) \tag{6}$$

and $J_n(z)$ is the Bessel function of the nth order. Formula (5) can be put into (2) only if the point r in (5) lies on the crystal surface. The first line in (5) is constructed in such a way that the formula

$$d^{(0)}(r) = \gamma_0 \int\limits_{S_e} dr'\,\hat{G}(r - r')\,D_e(r')\exp(-2\pi i\Delta . r) \tag{7}$$

is valid for the amplitudes of the waves on the entrance surface S_e of the crystal $[d_0^{(0)}(r) = D_e(r)\exp(-2\pi i\Delta . r)$ must hold]. The crystal is assumed to be semi-infinite, the waves are σ polarized. Green's function in the case when point r lies inside the crystal is more complicated (Afanas'ev & Kohn, 1971). It will be shown that it is not necessary to consider such an explicit form of Green's function.

As has been shown in the previous paper, if the coherent beam falls on the crystal with randomly distributed defects, the wavefield emitted from the crystal is a superposition of the coherent wave, which corresponds to the wave emitted from the quasiperfect crystal [the first term in (2)] and of the partially coherent wave (diffusion scattering) whose intensity depends on the covariance of the deformation field in the crystal. Thus, the presence of the correlation of the deformation field diminishes the degree of coherence of the emitted wave.

3. The first approximation of the diffracted intensity

We apply the general formula (2) for the computation of the first approximation of the intensity diffracted from the crystal containing randomly distributed amorphous spheres. The diameter of the spheres is R and their concentration (normalized to unity) is c. The polarizability coefficient χ'_h of the quasiperfect crystal is then given by $\chi_h \exp(-P)$ (cf. Holý, 1982b – referred to as II), where

$$P = 4c\pi R^3/(3V_c) \tag{8}$$

is the amorphous part of the crystal related to the whole crystal volume.

After some lengthy but easy algebra we obtain from (2) the following expression for the diffracted intensity

$$I_h^{(1)}(r_a) = I_h^{(0)} + M_1 + M_2, \tag{9}$$

where

$$M_1 = I_e \frac{\pi^2 K^2 |\chi_h|^2}{\sin^2 2\theta} \int\limits_V \int\limits_V dr\,dr'\,\exp[-2\pi i(\kappa . r - \kappa^* . r')]$$

$$\times N(r' - r)\,\delta(y_a - y)\,\delta(y_a - y')\,\delta(s_{0a} - s_0)$$

$$\times \delta(s_{0a} - s'_0)\,\Theta(s_{ha} - s_h)\,\Theta(s_{ha} - s'_h); \tag{10}$$

$$M_2 = \pi^2 K^2 \int\limits_V \int\limits_V dr\,dr'\,\exp[-2\pi i(\kappa . r - \kappa^* . r')]$$

$$\times \delta(y_a - y)\,\delta(y_a - y')\Bigg(N(r - r')|\chi_{-h}|^2$$

$$\times I_{hh}\,G'_{h0}(r_a - r)\,G'^*_{h0}(r_a - r')$$

$$+ N(r' - r)|\chi_h|^2 I_{00}\,G'_{hh}(r_a - r)\,G'^*_{hh}(r_a - r')$$

$$+ \frac{2I_{00}|\chi_h|^2}{\sin 2\theta}\,\mathrm{Re}[\delta(s_{0a} - s_0)\,\Theta(s_{ha} - s_h)$$

$$\times N(r' - r)\,G'^*_{hh}(r_a - r')]$$

$$+ 2\,\mathrm{Re}\{N'(r - r')\,\chi_{-h}\chi^*_h\,I_{h0}\,G'_{h0}(r_a - r)$$

$$\times [\delta(s_{0a} - s'_0)\,\Theta(s_{ha} - s'_h)/\sin 2\theta$$

$$+ G'^*_{hh}(r_a - r')]\}\Bigg). \tag{11}$$

The meaning of N, N', G'_{ij} is explained in II.

Let us consider first the term M_1. After some further rearrangement we obtain

$$M_1 = \tfrac{1}{4}K^2 |\chi_h|^2 I_e \frac{c}{V_c} \int\limits_{\substack{\text{reciprocal} \\ \text{space}}} dq \frac{|v(q)|^2}{|q_h - \kappa_h|^2} \tag{12}$$

where

$$v(q) = \int\limits_{\substack{\text{real} \\ \text{space}}} dr\{\exp[-2\pi i h . l(r)] - 1\}\exp(2\pi i q . r). \tag{13}$$

q_h, κ_h are the components of vectors q, κ, respectively, in the direction of the wavevector of the diffracted wave. $l(r)$ is the displacement caused by a single defect. For the crystal with randomly distributed amorphous spheres $v(q)$ was derived explicitly in II and the integral (12) was evaluated analytically (for details see Holý, 1982c).

$$M_1 = \pi R^3 K^2 \frac{c}{V_c} |\chi_h|^2 I_e \left\{ \frac{2\pi R}{|\text{Im } \kappa_h|} \right.$$

$$\times \text{Re} \left[\frac{1}{W^4} (2e^{iW}(iW - 1) + W^2 + 2) \right]$$

$$\left. + 1/(3|\kappa_h|^2) \right\} \qquad (14)$$

holds, where $W = 4\pi R \kappa_h$.

From the well known estimation of the value of a convolution (cf. Schwartz, 1965) the value of M_2 can be estimated. It can be shown that in the case of 333 Cu $K\alpha_1$ symmetrical diffraction on Si (Bragg case) the term M_2 makes at most 1% of M_1 if

$$PR^2 \leq 0.01 \ \mu\text{m}^2 \qquad (15)$$

holds. Then, M_2 can be completely neglected.

Let us consider the physical sense of such neglection. This neglection is equivalent to putting

$$\hat{G}(r_a - r) = \frac{\delta(y_a - y)}{\sin 2\theta}$$

$$\times \left\| \begin{matrix} \delta(s_{ha} - s_h) \, \Theta(s_{0a} - s_0) & 0 \\ 0 & \delta(s_{0a} - s_0) \, \Theta(s_{ha} - s_h) \end{matrix} \right\|$$

$$\qquad (16)$$

into (2). This expression for Green's function can be obtained by $\chi'_h \to 0$ in (5). It was shown in I that this limit yields the kinematical approximation of $\hat{G}$. Thus, the neglection of M_2 is equivalent to the assumption that the scattering of the wavefield in the crystal [the wavefield was computed dynamically – cf. (3)] can be described within the kinematical approximation. Thus, if (15) is valid, the partially coherent contribution to the reflection curve in the first approximation can be numerically evaluated from the explicit formula (14).

4. The second approximation of the diffracted intensity

In the previous chapter we showed that, if (15) is valid, the exact form of Green's function (5) can be replaced in (2) by its kinematical limit (16). The formula (5) for Green's function, however, cannot be used for exact computation of the second approximation of the intensity, because for this purpose we also need the values of $\hat{G}$ for the points r inside the crystal. From the paper of Afanas'ev & Kohn (1971) it follows that the

kinematical limit of Green's function is given by (16) for this case, too. Hence, if we restrict ourselves only to the kinematical approach for computing the second approximation of the diffracted intensity, which we have made already in the case of the first approximation, we need not use the exact form of Green's function inside the crystal.

The second approximation of the diffracted intensity is given by (I.54)

$$I_h^{(2)}(r_a) = I_h^{(1)}(r_a) + \exp[2\pi i(\Delta - \Delta^*) \cdot r_a]$$

$$\times \int_V \int_V dr dr' [\hat{\gamma}^{(0)}(r_a, r')$$

$$\times \langle \hat{p}^+(r') \hat{G}^+(r - r') \hat{p}^+(r) \rangle_E \hat{G}^+(r_a - r)$$

$$+ \hat{G}(r_a - r) \langle \hat{p}(r) \hat{G}(r - r') \hat{p}(r') \rangle_E$$

$$\times \hat{\gamma}^{(0)}(r', r_a)]. \qquad (17)$$

Deriving this formula we have neglected the third-order correlation terms $\langle \hat{G} \hat{p} \hat{\gamma}^{(0)} \hat{p}^+ \hat{G}^+ \hat{p}^+ \hat{G}^+ \rangle_E$ etc. Putting (4) and (16) into (17) we obtain, after some rearrangement,

$$I_h^{(2)} = I_h^{(1)} - \frac{K^2 I_{hh}}{2 \sin 2\theta} \frac{c}{V_c} \gamma_h \, \text{Re} \left(\frac{\chi_h \chi_{-h}}{\kappa_x \kappa_h} \left\{ 4\pi R^3 / 3 \right. \right.$$

$$\left. \left. - \frac{\gamma_h R^2}{\kappa_x \sin 2\theta} [(ie^{-iQ} - Qe^{-iQ} - i)/Q^2 - i/2] \right\} \right), \qquad (18)$$

where $Q = 4\pi \kappa_x R \sin 2\theta / \gamma_h$.

Comparing (18) with (14) we find that the first approximation of the partially coherent part of the diffracted intensity is proportional to the intensity of the primary beam while the contribution of its second approximation $I_h^{(2)} - I_h^{(1)}$ is proportional (in the approximation used) to the intensity diffracted by the quasiperfect crystal. The second approximation is therefore essential only in the region of the maximum of the reflection curve of the quasiperfect crystal. The assumption (16) results in a negligible error in the value of the second approximation if (15) is fulfilled.

5. Numerical results

Formulas (14) and (18) were used for the numerical evaluation of the first and second approximations of the diffracted intensity. The reflection curves were computed for 333 Cu $K\alpha_1$ symmetrical Bragg-case diffraction on Si, the defects were described by their diameter R and the relative amorphous volume P given by (8). Their values were chosen so as to fulfil condition (15).

The contributions of the first approximation to the reflection curve $\Delta I_h^{(1)}(\Delta\theta) = I_h^{(1)}(\Delta\theta) - I_h^{(0)}(\Delta\theta)$ and the reflection curve of the quasiperfect crystal $I_h^{(0)}(\Delta\theta)$ are plotted in Fig. 1 for various diameters R and various

concentrations c of defects so that the relative amorphous volume P remains constant. If R increases $\Delta I_h^{(1)}$ becomes narrower and higher. The minimum of $\Delta I_h^{(1)}$ in the position of the maximum of $I_h^{(0)}$ can easily be explained by the dependence of the effective absorption coefficient of X-rays on the departure $\Delta\theta$ from the Bragg position. Since the positions of the defects are not correlated, the partially coherent part of the reflection curve is proportional to the amount of irradiated defects and thus inversely proportional to this absorption coefficient. In the vicinity of the maximum of the coherent reflection curve $I_h^{(0)}(\Delta\theta)$ this absorption coefficient has a maximum and $\Delta I_h^{(1)}$ has a minimum. The asymmetry of the shape of $\Delta I_h^{(1)}$ is given by the asymmetry of the dependence of the effective absorption coefficient on $\Delta\theta$.

The contributions of the second iteration to the reflection curve $\Delta I_h^{(2)}(\Delta\theta) = I_h^{(2)}(\Delta\theta) - I_h^{(1)}(\Delta\theta)$ are plotted in Fig. 2 for various values of R and c so that P remains constant. These contributions are not negligible only in the vicinity of the maximum of $I_h^{(0)}$ where the absolute value of $\Delta I_h^{(2)}$ is comparable with $\Delta I_h^{(1)}$. For all angles of incidence $\Delta I_h^{(2)}$ is negative.

Integrating the functions $I_h^{(0)}(\Delta\theta)$, $\Delta I_h^{(1)}(\Delta\theta)$, $\Delta I_h^{(2)}(\Delta\theta)$ over $\Delta\theta$ in the range $(-\infty;\infty)$, we obtain the values $J_h^{(0)}$, $\Delta J_h^{(1)}$, $\Delta J_h^{(2)}$, respectively. $J_h^{(0)}$ is the integrated intensity of diffraction from the quasiperfect crystal, $\Delta J_h^{(1)}$ and $\Delta J_h^{(2)}$ are the contributions of the first and second approximations to the integrated intensity of diffraction. The dependences $J_h^{(0)}$, $\Delta J_h^{(1)}$, $\Delta J_h^{(2)}$ on the

diameter R (P remains constant) are plotted in Fig. 3 for various values of P. It is obvious that the contribution $\Delta J_h^{(1)}$ is practically not dependent on R if P remains constant. $\Delta J_h^{(2)}$, however, depends on R strongly but it makes at most a low percentage of $\Delta J_h^{(1)}$.

Fig. 4 shows the dependence of $J_h^{(0)}$, $\Delta J_h^{(1)}$, $\Delta J_h^{(2)}$ and of $J_h = J_h^{(0)} + \Delta J_h^{(1)} + \Delta J_h^{(2)}$ on P for a constant R. The dependence of $J_h^{(0)}$ on P is caused by the influence of P on χ_h'. Since the integrated intensity of diffraction from the quasiperfect crystal is proportional to $\mathrm{Re}\,\chi_h'$,

$$J_h^{(0)} \simeq J_h^{(\mathrm{perfect})}(1 - P) \qquad (19)$$

Fig. 2. The contributions of the second approximation $(\Delta I_h^{(2)})$ to the reflection curve computed for $P = 10^{-2}$ and R (a) 0·2 μm, (b) 0·4 μm, (c) 0·6 μm, (d) 0·8 μm, (e) 1·0 μm. The values of $\Delta I_h^{(2)}$ are negative.
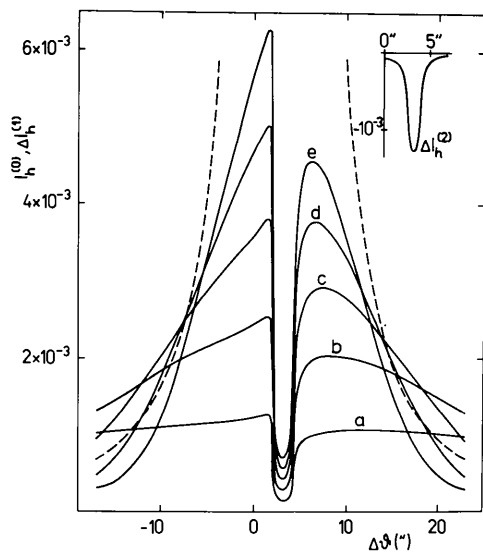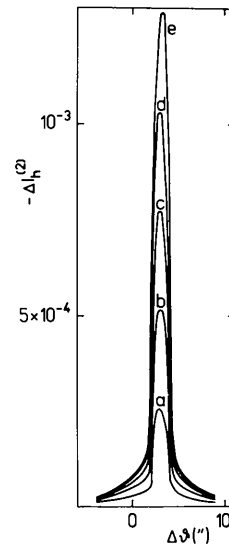
Fig. 1. The reflection curve (Cu $K\alpha_1$ 333 symmetrical Bragg case on Si) of the quasiperfect crystal ($I_h^{(0)}$ dashed line) and the contribution of the first approximation to the reflection curve ($\Delta I_h^{(1)}$ full line). The curves were computed for constant value of $P = 10^{-2}$, the values of R are (a) 0·2 μm, (b) 0·4 μm, (c) 0·6 μm, (d) 0·8 μm, (e) 1·0 μm. The contribution of the second approximation to the reflection curve ($\Delta I_h^{(2)}$) is plotted in the upper right corner for $R = 1·0$ μm, $P = 10^{-2}$. The intensities are normalized to the intensity of the primary beam.
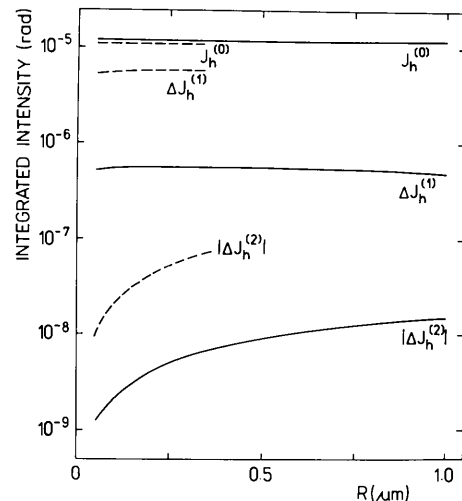
Fig. 3. The dependence of the integrated intensity of diffraction from the quasiperfect crystal ($J_h^{(0)}$) and of the contributions of the first and second approximations of the integrated intensity ($\Delta J_h^{(1,2)}$) on R for constant $P = 10^{-2}$ (full line) and 10^{-1} (dashed line).

holds. Thus, this dependence is approximately linear. The dependences of $\Delta J_h^{(1)}$, $\Delta J_h^{(2)}$ on P are given mainly by the fact that $\Delta J_h^{(1,2)}$ are proportional to c. The departures of this linear dependence are caused by the influence of P on χ_h' and thus on κ. For the values of P used, however, these deviations can be neglected and $\Delta J_h^{(1,2)}$ can be considered to be proportional to P.

6. Discussion

(i) During the computation we have restricted ourselves to the special form of the defects, namely, we have assumed that the defects are amorphous spheres which do not deform the surrounding lattice. The actual defects in the crystals, however, deform the lattice essentially. The displacement field caused by a single defect with a spherical symmetry can be written as (see Eshelby, 1956)

$$l(r) = \begin{cases} \dfrac{Ar}{|r|^3} & \text{for } |r| \geq R \\ \text{random value for } |r| < R, \end{cases}$$

where $4\pi A$ is the change in the crystal volume due to a single defect. If $|2\pi A h/R^2| < 1$ then the exponential function in (13) can be replaced by the first two terms of its Taylor series. Then the reflection curves can be evaluated analytically. It was shown (cf. Holý, 1982c) that the reflection curves obtained are asymmetrical and the asymmetry depends on the sign of A. The integrated intensities, on the contrary, depend on A only slightly. For greater values the reflection curves cannot be evaluated analytically.

(ii) Performing $\chi_h' \to 0$ in (12) we obtain from (12) an integral of $|v(q)|^2$ over the surface of the Ewald sphere near the reciprocal-lattice point, which represents

according to Dederichs (1971) the intensity of the diffusion scattering in the kinematical approximation. The angular distribution of the scattered intensity is then given directly by $|v(q)|^2$.

(iii) Comparison with the results of paper II shows that the shape of the incoherent contribution to the reflection curve in the Bragg case is similar to that of the Laue case.

7. Conclusions

The results obtained can be summarized into the following items:

(i) If the coherent plane wave falls on the crystal the diffracted wave is the superposition of the coherent plane wave which corresponds to the wave diffracted from the quasiperfect crystal and of the partially coherent wave whose MCF is dependent on the correlation of the deformation field in the crystal.

(ii) The partially coherent contributions to the reflection curve in the first and second approximations are proportional to the relative amorphous volume of the crystal and thus to the concentration of the defects. The first approximation of the reflection curve becomes narrower and higher if the diameter of the defects grows. The contribution of the second approximation is essential only in the close vicinity of the maximum of the reflection curve of the quasiperfect crystal and it is approximately proportional to the defect diameter.

(iii) The integrated intensity of diffraction from the quasiperfect crystal diminishes linearly with increasing the amorphous volume and it does not depend on the defect diameter. The first approximation of the partially coherent contribution to the integrated intensity is proportional to the amorphous volume and it is approximately not dependent on the defect diameter if this volume remains constant. The contribution of the second approximation to the integrated intensity is at most a few percent of the first approximation.
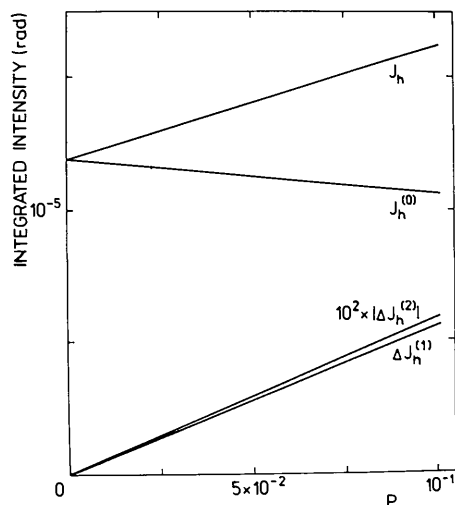

Fig. 4. The integrated intensities $J_h^{(0)}$, $\Delta J_h^{(1,2)}$ and the total integrated intensity J_h as a function of P for constant $R = 0\cdot3$ μm.

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