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Correction of Intensities of Diffraction Maxima for Absorption in Cylindrical Samples

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An analytical method is given for computing the correction factor, for the measured intensities of diffraction maxima, for absorption in cylindrical samples. The values of the transmission factor were calculated for the cases of a polycrystalline sample introduced into a cylindrical container and of a polycrystalline sample with annular cross section.

In neutron and X-ray diffraction in crystalline powders, the measured intensities of the diffraction maxima must be corrected for absorption in the sample. As the sample is often enclosed in a container, one has to take into account the different linear absorption coefficients of the sample and the container.

In neutronographic studies, where the samples have cylindrical shapes with diameters around 25 mm, the study of the transmission factor may contribute to the choice of optimum dimensions for the sample.

Determinations of the transmission factor in samples have so far been carried out by a graphical method (Møller & Jensen, 1952; Claassen, 1930) or an approximate calculation (Bradley, 1935). Neither allowed determination of an accurate value of the transmission factor.

The aim of this paper is to present a method of calculation for the transmission factor in cylindrical samples, with an accuracy limited only by the accuracy of the numerical calculation.

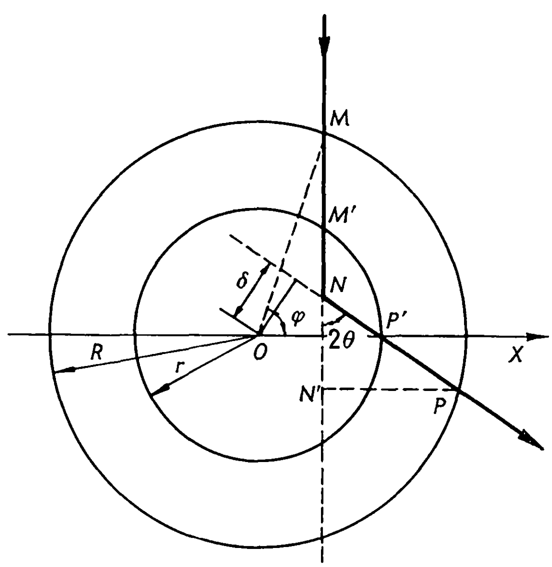

Fig. 1. φ and δ representation for calculation of the radiation path inside the sample.

Method of calculation

Consider a sample consisting of two media with different linear absorption coefficients, μ_1 and μ_2, enclosed by two coaxial cylindrical surfaces, of radii R and r ($r < R$) respectively. The incident beam falling upon the whole sample is scattered by the latter over an angle 2θ. Multiple scattering of the radiation within the sample is assumed to be negligible.

As shown in Fig. 1, if scattering occurs at a point N, the path of the radiation inside the sample is $MN+NP$.

The length of this path, Δ_0, can be expressed by means of the coordinates φ and δ, φ being the angle between the position vector of point M and the OX direction (we denote by M the intersection of the incident ray passing through point N with the sample boundary), and δ the distance from the origin to the scattering direction passing through point N. φ can vary between the limits 0 and π, and the variable δ between the limits $R\cos(\varphi-2\theta)$ and $R\cos(\varphi+2\theta)$.

$$\Delta_0 = \frac{\delta_{\max}-\delta}{\sin 2\theta} + \frac{NN'}{\cos 2\theta}\,. \tag{1}$$

Simple geometrical considerations allow us to express relation (1) as a function of the variables φ and δ:

$$\Delta_0 = R\,[\sin\varphi - \text{tg}\,\theta\cos\varphi - (\delta/R)\,\text{tg}\,\theta + \sqrt{(1-(\delta/R)^2)}]\,. \tag{2}$$

The path Δ_0 of the radiation inside the sample can be expressed as the sum of two components, corresponding to the two media with different linear absorption coefficients. With the notations $x=\delta/R$ and $\Phi = \text{arc}\cos(\cos\varphi/\beta)$, $\beta = r/R$, one may write:

$$\begin{aligned}\Delta_0 &= \Delta_{01}+\Delta_{02}\\ \Delta_{01} &= MM'+PP' = \Delta_0-\Delta_{02}\end{aligned} \tag{3}$$

where

$$\Delta_{02} = M'N + NP'$$
$$= R\beta\,[\sin\Phi - \mathrm{tg}\,\theta\cos\Phi - (x/\beta)\,\mathrm{tg}\,\theta + \sqrt{(1-(x/\beta)^2)}].$$

The transmission factor of the polycrystalline sample may be expressed as the sum of two terms: the first represents the fraction of neutrons scattered over an angle 2θ by the medium of linear absorption coefficient μ_1 which, before leaving the sample, have travelled either only through this medium or through both media, while the second term represents the fraction of neutrons scattered over the same angle by the medium of linear absorption coefficient μ_2 which, before leaving the sample, have travelled through both media.

The expression for the transmission factor will therefore be:

$$A = \frac{1}{\pi(1-\beta^2)\sin 2\theta}\sum_i \int_{\varphi_{1i}}^{\varphi_{2i}} \sin\varphi\, d\varphi \times \int_{x_{\min i}}^{x_{\max i}} \exp\left[-\mu_1\Delta_{01i}(x,\varphi,\theta) - \mu_2\Delta_{02i}(x,\varphi,\theta)\right]dx$$
$$+ \frac{1}{\pi\beta^2\sin 2\theta}\int_{\Psi}^{\pi-\Psi}\sin\varphi\, d\varphi \times \int_{-\sqrt{(\beta^2-\cos^2\varphi)}}^{\sqrt{(\beta^2-\cos^2\varphi)}} \exp\left[-\mu_1\Delta_{01}(x,\varphi,\theta) - \mu_2\Delta_{02}(x,\varphi,\theta)\right]dx, \quad (4)$$

where $\psi = \arccos\beta$, and the factors which multiply the two sums represent the normalizing factor of the beam scattered over the angle 2θ to the incident beam. The first term of the transmission factor is a sum because the neutrons may pass through the sample in both ways mentioned above. Numerical calculation of expression (4) requires division of the sample into regions defined by the way in which the radiation travels through the sample and by the range of variation of the two variables. Fig. 2 shows the

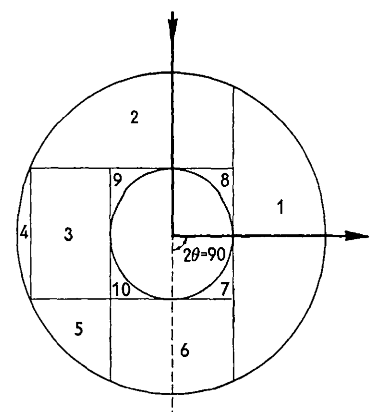

Fig. 2. Integration domains for the case $2\theta = 90°$ and $\beta = 0{\cdot}4$.

integration domains for case $2\theta = 90°$ and $\beta = 0{\cdot}4$, and Table 1 contains the integration limits and the

Table 1. *Integration limits and exponent expression of the function under the integral sign for the sum components in relation* (4), *for* $\mu_2 = 0$, $2\theta = 90°$, $\beta = 0{\cdot}4$

Zone	Integration limits: φ_{1i}	φ_{2i}	$x_{1i}(t_{1i}, \varepsilon_{1i})$	$x_{2i}(t_{2i}, \varepsilon_{2i})$	Exponent expression
1	0	ψ	$\lvert 2\theta-\varphi\rvert$	$2\theta+\varphi$*	$-\alpha(\sin\varphi-\cos\varphi+\sin t-\cos t)$
2	ψ	$2\theta+\psi$	$\lvert 2\theta-\varphi\rvert$	ψ*	$-\alpha(\sin\varphi-\cos\varphi+\sin t-\cos t)$
3	$\pi-\psi$	$2\theta+\psi$	$-\beta$	β	$-\alpha(\sin\varphi-\cos\varphi+\sqrt{(1-x^2)}-x-2\sqrt{(\beta^2-x^2)})$
4	$2\theta+\psi$	π	$\varphi-2\theta$	$2\pi-(2\theta+\varphi)$*	$-\alpha(\sin\varphi-\cos\varphi+\sin t-\cos t-2\sqrt{(\beta^2-\cos^2 t)})$
5	$\pi-\psi$	$2\theta+\psi$	$\pi-\psi$	$2\pi-(2\theta+\varphi)$*	$-\alpha(\sin\varphi-\cos\varphi+\sin t-\cos t)$
6	ψ	$\pi-\psi$	$\pi-\psi$	$\pi-\lvert\varphi-2\theta\rvert$*	$-\alpha(\sin\varphi-\cos\varphi-2\sqrt{(\beta^2-\cos^2\varphi)}+\sin t-\cos t)$
7	ψ	$\pi-$ arc cos $(\beta\cos 2\theta)$	$2\theta+$ arc cos $(\cos\varphi/\beta)$	π†	$-\alpha(\sin\varphi-\cos\varphi-2\sqrt{(\beta^2-\cos^2\varphi)}+\sqrt{(1-\beta^2\cos^2\varepsilon)}-\beta\cos\varepsilon)$
8	ψ	arc cos $(\beta\cos 2\theta)$	0	$2\theta-$ arc cos $(\cos\varphi/\beta)$†	$-\alpha(\sin\varphi-\cos\varphi+\sqrt{(1-\beta^2\cos^2\varepsilon)}-\beta\cos\varepsilon)$
9	arc cos $(\beta\cos 2\theta)$	$\pi-\psi$	0	arc cos $(\cos\varphi/\beta)$ -2θ†	$-\alpha(\sin\varphi-\cos\varphi+\sqrt{(1-\beta^2\cos^2\varepsilon)}-\beta\cos\varepsilon-2\beta\sin\varepsilon)$
10	$\pi-$ arc cos $(\beta\cos 2\theta)$	$\pi-\psi$	$2\pi-2\theta-$ arc cos $(\cos\varphi/\beta)$	π†	$-\alpha(\sin\varphi-\cos\varphi-2\sqrt{(\beta^2-\cos^2\varphi)}+\sqrt{(1-\beta^2\cos^2\varepsilon)}-\beta\cos\varepsilon-2\beta\sin\varepsilon)$

* $t = \arccos x$. † $\varepsilon = \arccos(x/\beta)$.

exponent of the function under the integral sign for the sum components in expression (4) for $\mu_2=0$. In this case, the second term in (4) vanishes, since the radiation is no longer scattered in the second medium.

Since in the expressions of Δ_0 and Δ_{02}, the radius R of the sample studied appears as a factor, the quantities $\alpha_1=\mu_1 R$ and $\alpha_2=\mu_2 R$ will be chosen instead of the two linear absorption coefficients as parameters for the numerical calculation. Hence, estimation of expression (4) will be made for the parameters α_1, α_2, β and θ, depending upon the composition of the target, upon its dimensions and upon the scattering angle.

Numerical calculation of the transmission factor

The numerical calculation of (4) was made for two cases:

(*a*) For a polycrystalline sample obtained by introducing the material under study into a container made of a different material.

(*b*) For a polycrystalline sample of annular cross section.

In both cases the calculation was made with a digital computer, the integrals in (4) having an analytical form.

In case (*a*) the transmission factor was tabulated for the following values of the parameters: $\alpha_1=0{\cdot}4$; $\alpha_2/\alpha_1=0$; $0{\cdot}1$; $0{\cdot}5$; 1; 10; $\beta=0{\cdot}95$; $2\theta=90°$. The results obtained are plotted in Fig. 3. It will be noticed that for the value 1 of the ratio α_2/α_1, the transmission factor has the value 0·53. For values of this ratio smaller than unity, the transmission factor increases rather quickly, reaching the value 0·93 for $\alpha_2/\alpha_1=0$.

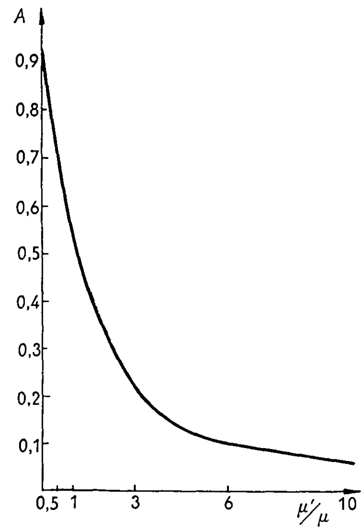

Fig. 3. Plot of the transmission factor *versus* μ_2/μ_1 for $2\theta=90°$, $\beta=0{\cdot}95$.

The value 0·4 for the parameter α_1 was obtained for a cylindrical copper container, 40 mm in diameter and of a wall thickness 1 mm, used for neutronographic study. (The linear absorption coefficient for copper

Table 2. *Transmission factors for a polycrystalline sample with annular cross section for scattering angles of* 0°, 45°, 90°, 135° *and* 180°

$2\theta=0°$

α \ β	0	0·2	0·4	0·6	0·8	0·9	0·95
0·2	0·714	0·725	0·756	0·806	0·878	0·926	0·958
0·4	0·512	0·528	0·574	0·652	0·775	0·862	0·921
0·6	0·370	0·386	0·437	0·529	0·685	0·804	0·886
0·8	0·269	0·284	0·334	0·431	0·607	0·751	0·852
1·0	0·196	0·210	0·256	0·352	0·539	0·702	0·821
1·5	0·092	0·102	0·134	0·214	0·404	0·596	0·748
2·0	0·046	0·051	0·072	0·133	0·306	0·509	0·685
2·5	0·024	0·028	0·040	0·083	0·234	0·435	0·628
3·0	0·013	0·016	0·023	0·053	0·180	0·378	0·578
3·5	0·008	0·009	0·014	0·034	0·140	0·327	0·533

$2\theta=45°$

α \ β	0	0·2	0·4	0·6	0·8	0·9	0·95
0·2	0·716	0·727	0·758	0·808	0·878	0·927	0·957
0·4	0·518	0·533	0·578	0·656	0·774	0·862	0·918
0·6	0·379	0·395	0·445	0·536	0·685	0·802	0·882
0·8	0·280	0·295	0·344	0·440	0·608	0·748	0·847
1·0	0·209	0·224	0·269	0·363	0·540	0·699	0·814
1·5	0·106	0·119	0·151	0·229	0·408	0·593	0·740
2·0	0·059	0·069	0·090	0·150	0·312	0·506	0·673
2·5	0·038	0·044	0·058	0·101	0·242	0·435	0·613
3·0	0·027	0·030	0·039	0·070	0·189	0·367	0·559
3·5	0·022	0·023	0·029	0·051	0·150	0·300	0·511

Table 2 (*cont.*)

$2\theta=90°$

α \ β	0	0·2	0·4	0·6	0·8	0·9	0·95
0·2	0·719	0·732	0·760	0·808	0·878	0·925	0·954
0·4	0·529	0·546	0·581	0·660	0·766	0·856	0·914
0·6	0·398	0·416	0·455	0·541	0·679	0·795	0·876
0·8	0·307	0·323	0·367	0·450	0·600	0·739	0·840
1·0	0·242	0·253	0·298	0·375	0·533	0·689	0·806
1·5	0·146	0·157	0·186	0·249	0·412	0·581	0·730
2·0	0·099	0·107	0·127	0·177	0·332	0·495	0·664
2·5	0·073	0·078	0·092	0·131	0·260	0·416	0·602
3·0	0·058	0·061	0·071	0·100	0·214	0·342	0·548
3·5	0·048	0·050	0·058	0·081	0·175	0·285	0·502

$2\theta=135°$

α \ β	0	0·2	0·4	0·6	0·8	0·9	0·95
0·2	0·727	0·736	0·764	0·810	0·880	0·927	0·955
0·4	0·547	0·559	0·597	0·666	0·777	0·860	0·911
0·6	0·425	0·436	0·477	0·554	0·690	0·796	0·874
0·8	0·340	0·352	0·390	0·467	0·616	0·741	0·839
1·0	0·279	0·288	0·325	0·398	0·553	0·692	0·807
1·5	0·186	0·196	0·224	0·282	0·431	0·588	0·736
2·0	0·137	0·142	0·164	0·212	0·363	0·505	0·669
2·5	0·107	0·112	0·129	0·167	0·293	0·438	0·618
3·0	0·086	0·090	0·103	0·135	0·250	0·387	0·572
3·5	0·064	0·071	0·082	0·108	0·214	0·347	0·531

$2\theta=180°$

α \ β	0	0·2	0·4	0·6	0·8	0·9	0·95
0·2	0·728	0·738	0·766	0·812	0·881	0·928	0·959
0·4	0·552	0·565	0·605	0·673	0·784	0·867	0·921
0·6	0·435	0·448	0·489	0·567	0·703	0·812	0·887
0·8	0·353	0·366	0·406	0·485	0·635	0·763	0·855
1·0	0·295	0·306	0·343	0·420	0·576	0·719	0·826
1·5	0·205	0·214	0·243	0·309	0·463	0·626	0·760
2·0	0·155	0·163	0·186	0·240	0·383	0·551	0·703
2·5	0·126	0·131	0·150	0·195	0·323	0·491	0·653
3·0	0·105	0·110	0·125	0·164	0·278	0·441	0·610
3·5	0·090	0·094	0·108	0·141	0·243	0·399	0·571

is 0·18 cm^{-1} in the range of thermal neutrons.) The results obtained show that the choice of aluminum as container material (μ_{Al} = 0·008 cm^{-1}) practically enables one in most cases to neglect the contribution of the container walls to the transmission factor.

In case (*b*), relation (4) was tabulated for the following values of the scattering angle 2θ: 0°; 45°; 90°; 135°; 180°. The following values were chosen for the parameters α and β, for each of the above values of the scattering angle: α=0·2; 0·4; 0·6; 0·8; 1; 1·5; 2; 2·5; 3; 3·5; β=0; 0·2; 0·4; 0·6; 0·8; 0·9; 0·95. The results obtained are shown in Table 2. To illustrate the variation of the transmission factor with α and β, the dependency of the transmission factor on α and β respectively for $2\theta=90°$ is shown in Figs. 4 and 5. As can be seen from the tables, for $\beta=0$, the values calculated starting from expression (4) are in good agreement with the tabulated data obtained by other methods (*International Tables for X-ray Crystallography*, 1959).

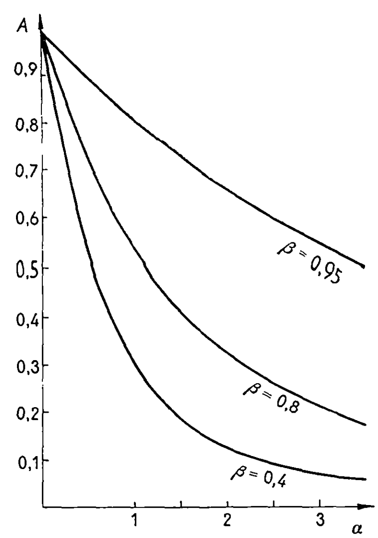

Fig. 4. Transmission factor *versus* $\mu_1 R$ for case $\mu_2=0$, $2\theta=90°$.

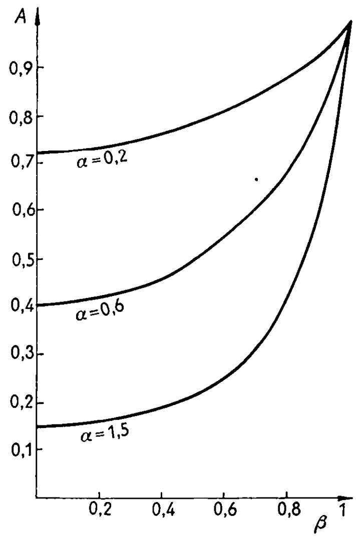

Fig. 5. Transmission factor *versus* r/R for case $\mu_2=0$, $2\theta=90°$.

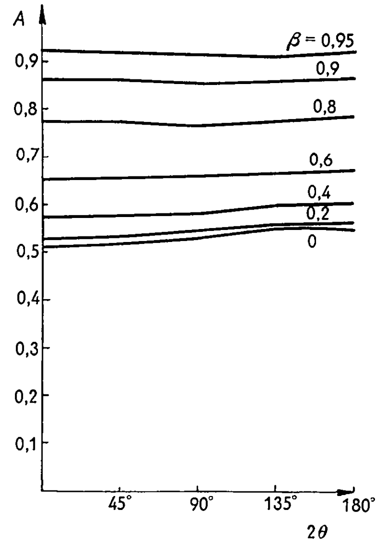

Fig. 6. Transmission factor *versus* scattering angle for case $\mu_2=0$, $\mu_1R=0{\cdot}4$.

Graphs like those in Figs. 4 and 5 allow optimum dimensions to be chosen for the target, from the standpoint of the transmission factor in diffraction studies. They also allow the value of the transmission factor to be found for non-tabulated α and β values, by an interpolation method.

Fig. 6 shows a plot of the transmission factor *versus* scattering angle for $\alpha=0{\cdot}4$ and for various values of the parameter β. The smallness of its variation with the scattering angle makes it easy to find, by interpolation, the values of the transmission factor for other scattering angles.

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Ordering in Binary σ Phases

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An X-ray diffraction study has been made of the ordering of atoms in the following binary σ phases: NbOs, NbIr, NbRe, MoOs, MoIr and CrRe. Ordering of atoms among the different atomic sites has been shown to exist in all cases. From these results and others it is deduced that the size of the constituent atoms is a major factor in governing the filling of A, B, and D sites but in addition some valency electron factor governs the filling of C and E sites.

Introduction

Considerable work has been done in recent years on binary σ phases involving transition metals of all three long periods. Comprehensive surveys on the stability and composition of these phases have been carried out by Knapton (1958) and Greenfield & Beck (1956), but most of this work has been confined to phases involving elements in the first and second long periods. This report is concerned with an X-ray diffraction investigation of the order involved in additional σ phases consisting of elements of the second and third long periods: NbOs, NbIr, NbRe, MoOs, MoIr, WOs and in addition, a σ phase of particular interest: CrRe.