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Cristallografia. — *Absorption correction for some elongated prismatic crystals.* Nota di ELIO CANNILLO e FIORENZO MAZZI (*), presentata (**) dal Socio G. CAROBBI.

RIASSUNTO. — Si danno tre formule generali per il calcolo del fattore di trasmissione dei raggi X, da usarsi nelle ricerche di cristallografia strutturale durante la correzione delle intensità degli effetti di diffrazione.

L'uso di tali formule è limitato a cristalli prismatici allungati aventi sezione a forma di parallelogramma, allorché la ripresa è fatta secondo la tecnica di Weissenberg con equi-inclinazione e solo la parte centrale del prisma costituente il cristallo è completamente bagnata dai raggi X incidenti.

Le formule permettono la risoluzione completa dell'integrale del fattore di trasmissione e non semplicemente la sua valutazione per punti.

Si dà la descrizione di un programma, preparato in particolare per il calcolatore Olivetti Elea 6001, che, partendo dalle costanti reticolari del cristallo, dalle dimensioni della sua sezione e dal coefficiente di assorbimento lineare, permette al calcolatore, dopo avere valutato l'orientamento dei raggi X incidenti e diffratti da ogni serie di piani reticolari, di scegliere fra le tre formule quella adatta, di semplificarla adeguatamente e di eseguire infine il calcolo del fattore di trasmissione.

During the elaboration of the intensity data obtained from a prismatic crystal, we have derived some formulae for the calculation of the transmission factor also suitable for their direct elaboration in an electronic computer. The main features of these formulae are as follows:

(1) they are usable for the calculation of the transmission factor for the reflections derived from equi-inclination Weissenberg photographs of elongated prismatic crystals (rotation axis parallel to the elongation axis), the cross section of which is a parallelogram, and when only the central part of the crystal is completely bathed by the X-ray beam, whereas the extremities of the prism are not reached by the beam itself;

(2) the formulae have been obtained with the resolution of the integral of the transmission factor; for the experimental conditions written above, the integration may be carried out in two dimensions on the area covered by the cross section of the crystal also for the reflections of the upper levels;

(3) no limitation to their application is due to the value of the linear absorption coefficient μ.

We think worthwhile to give a brief account of these formulae and their practical application, even if their use is confined to crystals of a particular habit, which is not however infrequent in X-ray works.

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Fig. 1 A) shows the cross section of the crystal of edges *a* and *b*; ω ($0^o < \omega < 180^o$) is the angle between the edges. The incident beam MD enters the crystal from the vertex M and its direction is comprised between the edge MQ and the diagonal MP. Also in fig. 1 A) and, in more detail, in fig. 1 B), are drawn the directions of ten diffracted rays, leaving the crystal from one of the four vertices: such directions represent ten possible instances and each of them is included between special directions defined either by

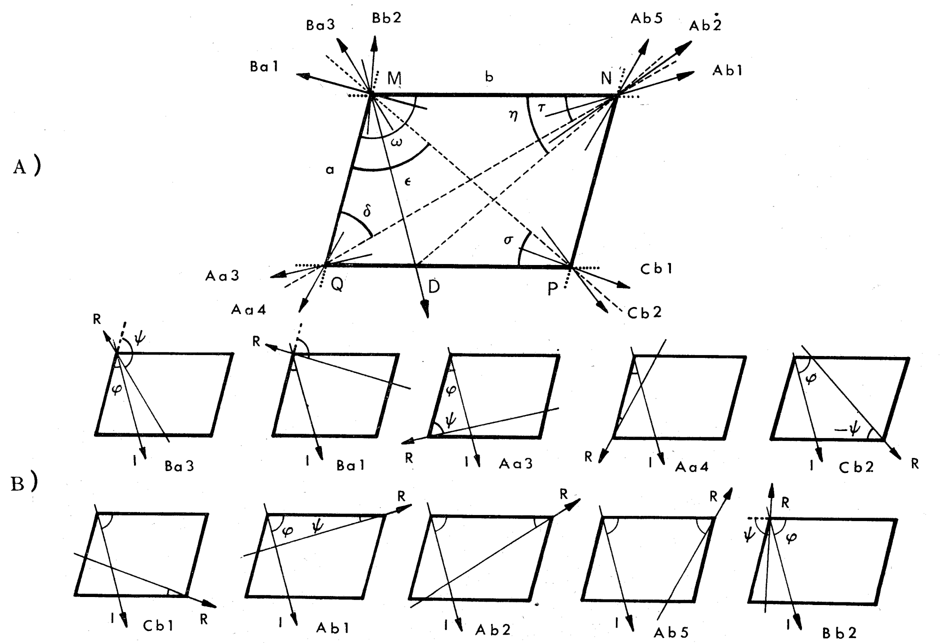

Fig. 1.

A) The standard case for the incident beam and the ten possible directions of the diffracted rays; B) The angles φ and ψ used in the calculations for each of the cases of fig. 1 A).

the cross section edges or diagonals as well as the particular direction DN (D being the point of intersection between the direct beam MD and the edge QP).

The ten cases are divided in two groups: group *a* if the direction of the reflected beam is to the left of the incident beam, group *b* if it is on the right side. The angles φ and ψ are those used for the calculations and they represent respectively the angles between either the direction of the incident beam or that of the diffracted beam with respect to one of the edges of the cross section: edge *a* for the former group mentioned above, edge *b* for the latter. In turn the ten instances are also classified into A, B, C classes: A when the diffracted rays leave the crystal from vertices Q or N, B and C respectively for diffracted rays going out from vertices M and P. We distinguish in such way five directions of diffracted rays classified A (A*b*1, A*b*2, A*a*3, A*a*4, A*b*5), three classified B (B*a*1, B*b*2, B*a*3), and two C (C*b*1, C*b*2). The possible case Ca2 may be treated as a C*b*2.

From the fig. 1 B) one can see that the straight lines corresponding to the direct and diffracted rays divide the cross section of the crystal into three or four portions. An incident beam which arrives at any point included in the same portion enters the cross section of the crystal from the same edge; so also a diffracted beam departing from any point of the same portion leaves the cross section from the same edge.

If one assumes as parametric axes those corresponding to the edges of the cross section, assigning to them a positive sense corresponding to the assumed value of angle ω, it is possible to represent, in each of the portions into which the cross section has been divided, the total path t of the rays diffracted in a point as a function of the parameters x , y of the point itself, the constants a, b, ω of the cross section and the angles φ and ψ.

For each portion, assuming the corresponding limits, it is thus possible to derive a formula representing the integral $\int \exp(-t\,\mu/\cos\nu)\,dx\,dy \sin\omega$ (ν is the equi-inclination angle). Summing up the results obtained from each portion and dividing the results both for $ab \sin\omega$ (area of the cross section, because the calculation is reduced to a two-dimensional case) and $\cos\nu$, we obtain the formula for the transmission factor for any equi-inclination Weissenberg level.

We found that the final results can be represented by only three general formulae corresponding respectively to each of classes A, B, C. If

$V = \cos\nu/(\mu \sin\omega)$, $1/W = \sin\varphi + \sin\psi$, $1/X = \sin(\omega+\psi) - \sin(\omega-\varphi)$, $c = V\sin\varphi$, $d = V\sin\psi$, $f = V\sin(\omega-\varphi)$, $g = V\sin(\omega+\psi)$, $m = VW\sin\varphi\sin\psi$, $n = VW\sin(\omega-\varphi)\sin\psi$, $p = VW\sin(\omega+\psi)\sin\varphi$, $q = VX\sin(\omega-\varphi)\sin(\omega+\psi)$, $r = VX\sin(\omega-\varphi)\sin\psi$, $s = VX\sin\varphi\sin(\omega+\psi)$, $z = n + p$, $u = r + s$, $v = a/u + b/z$, $1/S = ab\cos\nu$, the three formulae are respectively for classes Ab, Ba and Cb:

Ab $S\,[(bm + dn + cp - zm) + K_1(zm + gm + dq - dn - gs - uq)\exp(-b/z) + K_2(gs + qs)\exp(-a/s - b/g) - K_3\,cg\exp(-a/c) + K_4(aq + qr - br - dq)\exp(-b/g) - K_5\,df\exp(-a/d) + K_6(qr - fr)\exp(-b/f + a/r) + K_7(bs + qs + cq - aq)\exp(-b/f) + K_8(az + fm + mn + mp + gm - bm)\exp(-a/m)]$;

Ba: $S\,[(am + bq + qr + dn - dq - mn) + K_1(fr - qr)\exp(b/r) + K_2\,df\exp(-a/f - b/d) + K_3(mn - dn)\exp(-a/n) + K_4(bn + mn + fm - am)\exp(-b/m) + K_5(dq - qr - ar - bq)\exp(-a/q)]$;

Cb: $S\,[(cg - df) + (mz + fm + an - bm - cp)\exp(-a/c) + K_1(uq + gs - fm - gm - zm - fr)\exp(-v) + K_2(aq + br + dq - gs - uq)\exp(-b/g) + K_3(ap + bm + dn - gm - zm)\exp(a/d)]$.

In these formulae K_1 , K_2 , $\cdots$, K_8 are constants and they assume either the values 1 or 0 according to each of ten possible directions of diffracted beams in the way we shall explain. The same formulae are in turn valid for the classes Aa, Bb, with simple changes, as will be shown below.

We prepared a Fortran program suitable for our computer Olivetti Elea 6001 in order to carry out the calculation of the three final formulaè. The program needs the following initial data: 1) the unit cell parameters, 2) the constants of the cross section of the crystal: a, b (cm), $\cos \omega$ and the direction cosines of its edges in respect to the crystallographic axes, 3) the linear absorption coefficient μ. The calculation is accomplished through the following steps:

1) for each reflection the program estimates the direction cosines of the projections respectively of the incident beam ($\cos I\frown a$, $\cos I\frown b$) and of the reflected beam ($\cos R\frown a$, $\cos R\frown b$) on the plane of the cross section of the crystal for respect to its edges a and b;

2) the program reduces all the possible instances to the standard case of fig. 1 A), as far as the direction of incident beam is concerned;

3) the following step is the identification of the vertex of the cross section from which the reflected beam is going out. The four classes Aa, Ab, B and C are so distinguished;

4) within each of these instances the further distinction of each of the ten possibilities for the direction of diffracted beam is accomplished, the proper values for φ, ψ, a, b and constants K_n are assigned, then the program is addressed to the final formulae for the calculation of the transmission factor. Table I. summarizes steps 2, 3, 4.

The final formulae are valid also in particular cases when either the incident beam or the diffracted beam are parallel to the edges or the diagonals of the cross section, provided that the program, in order to avoid divisions by zero, does not calculate the values of the exponentials for the terms in which the costants K_n are zero. The final formulae are not valid when $\sin(\omega - \varphi) = \sin(\omega + \psi)$: this case (class A of reflected beams) is fairly frequent for rectangular cross sections ($\omega = 90°$), when $\varphi = \psi$ (reflecting planes parallel to the edges of the cross section). In such a circumstance the program does not estimate the values $1/X$, q, r, s, u, v, and, after the calculation of $h = \sin\varphi/\sin(\omega - \varphi)$, $l = \sin\psi/\sin(\omega + \psi)$, $Z = bm + dn + cp - fm$, uses the following formulae according to the different cases:

Ab1: $S\,[Z - cf \exp(-a/c) + (3fm - df - af + 2\,bm - bd + a^2/2\,h - b^2\,ml/2\,c) \exp(-b/f)]$;

Ab2: $S\,[Z - cf \exp(-a/c) - df \exp(-a/d) + (3fm - 2\,af + 2\,bm + a^2f/2\,m + b^2m/2f - ab) \exp(-b/f)]$;

Ab3: $S\,[Z - df \exp(-a/d) + (3fm - cf - af + 2\,bm - bc + a^2/2\,l - b^2\,hm/2\,d) \exp(-b/f)]$;

Ab4: $S\,[Z + (3fm - cf - df + 2\,bm - bc - bd + b^2m/2f - b^2c/2p + ab) \exp(-b/f)]$;

Ab5: $S\,[Z - cf \exp(-a/c) - df \exp(-a/d) + (3fm + af - bm) \exp(-a/m)]$.

TABLE I.

Values of cosines (sign + means no change in the original sign)

STEP 2 (a)	$\cos I^\frown a$	$\cos R^\frown a$	$\cos I^\frown b$	$\cos R^\frown b$	$\cos\omega$	
$\sin(I^\frown a + I^\frown b) = \sin\omega$	+	+	+	+	+	
$= -\sin\omega$	—	—	—	—	+	
$\sin(I^\frown a - I^\frown b) = \sin\omega$	—	—	+	+	—	
$= -\sin\omega$	+	+	—	—	—	

STEP 2 (b)						
$\cos I^\frown a \geq \cos\varepsilon$	+	+	+	+	+	$a \rightleftarrows b$
$\cos I^\frown a < \cos\varepsilon$	$\cos I^\frown b$	$\cos R^\frown b$	$\cos I^\frown a$	$\cos R^\frown a$	+	

STEP 3	*Classes of reflected beams*
$\sin(R^\frown a + R^\frown b) = \sin\omega$	C
$= -\sin\omega$	B
$\sin(R^\frown a - R^\frown b) = \sin\omega$	A*b*
$= -\sin\omega$	A*a*

STEP 4

Classes of reflected beams — *Constants to be inserted in the final formulae*

Classes of reflected beams	φ	ψ	a	b	K_1	K_2	K_3	K_4	K_5	K_6	K_7	K_8	*final formulae*
C													
$\cos R^\frown b \geq \cos\sigma$ yes (C*b* 1)	$I^\frown b$	$-R^\frown b$	a	b	1	1	0	=	=	=	=	=	C*b*
$\cos R^\frown b \geq \cos\sigma$ no (C*b* 2)					0	0	1	=	=	=	=	=	
B													
$\cos R^\frown a < -\cos I^\frown a$ yes (B*b* 2)	$I^\frown b$	$R^\frown b$	b	a	1	0	0	1	0	=	=	=	B*a*
no: $\cos R^\frown a \leq -\cos\varepsilon$ yes (B*a* 3)	$I^\frown a$	$R^\frown a$	a	b	0	0	1	0	1	=	=	=	
no: $\cos R^\frown a \leq -\cos\varepsilon$ no (B*a* 1)					1	1	1	0	0	=	=	=	
A*b*													
$\cos R^\frown b \geq \cos\tau$ yes (A*b* 1)	$I^\frown b$	$R^\frown b$	a	b	1	1	1	1	0	0	0	0	A*b*
no: $\cos R^\frown b \geq \cos\eta$ yes (A*b* 2)					1	1	1	0	1	1	0	0	
no: $\cos R^\frown b \geq \cos\eta$ no (A*b* 5)					0	0	1	0	1	0	0	1	
A*a*													
$\cos R^\frown a \geq \cos\delta$ yes (A*a* 4)	$I^\frown a$	$R^\frown a$	b	a	1	0	0	1	0	0	1	0	
$\cos R^\frown a \geq \cos\delta$ no (A*a* 3)					1	0	0	0	1	1	1	0	

$$\cos\varepsilon = \frac{a + b\cos\omega}{\sqrt{a^2 + b^2 + 2ab\cos\omega}} \; ; \quad \cos\sigma = \frac{b + a\cos\omega}{\sqrt{a^2 + b^2 + 2ab\cos\omega}} \; ; \quad \cos\delta = \frac{a - b\cos\omega}{\sqrt{a^2 + b^2 - 2ab\cos\omega}} \; ; \quad \cos\tau = \frac{b - a\cos\omega}{\sqrt{a^2 + b^2 - 2ab\cos\omega}}$$

$$\cos\eta = \frac{b \operatorname{sen} I^\frown b - a\cos I^\frown b \operatorname{sen}\omega}{\sqrt{a^2 \operatorname{sen}^2\omega + b^2 \operatorname{sen}^2 I^\frown b - ab \operatorname{sen} 2\, I^\frown b \operatorname{sen}\omega}}$$

The described procedure, after a control with data obtained with the graphical method by Albrecht (Smith, 1959) [2], has been successfully adopted for the computation of the absorption coefficients of a prismatic crystal of krauskopfite (Coda *et al.*, 1967) [1].

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