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On the Absorption Corrections of Single-Crystal X-Ray Data

Influence of Absorption Errors in the Structure Determination of BiOF

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A number of absorption correction programs have been constructed for the electronic computers BESK and FACIT EDB. The influence of absorption errors is discussed here in connection with a specific example, the structure determination of BiOF.[1]

Due to the availability of fast digital computers, it is possible to make absorption corrections without unreasonably cumbersome hand calculations. The author has therefore written a number of absorption correction programs for the electronic computers BESK and FACIT EDB. The main principles used are well known from the works of Busing and Levy [2] and Wells.[3] The programs are thoroughly tested and have been used in several cases.

The absorption programs are applicable to Weissenberg, precession, and goniostat data. It is assumed that the crystal can be described by $n \leq 14$ plane surfaces. A coordinate system is chosen with the origin inside the crystal. Each surface is written as an inequality

$$ax + by + cz + d < 0$$

with the coefficients a, b, c, d chosen so that the inequality is satisfied only if the points (0,0,0) and (x,y,z) lie on the same side of the surface. The crystal must have no re-entrant angles. The factor computed is

$$A = \frac{1}{V_0}\int_0^{V_0} e^{-\mu r}\, dV$$

where V_0 is the volume of the crystal, μ is the linear absorption coefficient, and r is the path length along the beam. The units must be chosen so that μr is dimensionless. The integral is evaluated numerically using the method of Gauss.[4,5] If the number of volume elements used during the integration is

denoted by m^3, the restriction depending on the capacity of the computer may be written $(n + 1)\, m^3 < 8000$. In the case of absorption corrections for intensities measured from precession photographs, the numerical integration is somewhat complicated by the fact that each reciprocal lattice point reflects twice, once as the point passes into the sphere of reflection and once as it passes out. In the general case this will give two different A values and the arithmetic mean of these must therefore be calculated. Further details concerning the programs are given in a document,[6] reprints of which are available upon request from this Institute.

Among the applications of these programs the corrections of X-ray intensities from a single crystal of BiOF have given some useful information on absorption errors and on the calculation of absorption factors. The following discussion is therefore based on data from the structure determination of BiOF. The structure was determined by Aurivillius.[1]

The intensities of X-ray reflections from a single crystal of BiOF were measured visually from precession photographs. The crystal used may be described as a thin square plate with the edges $225 \times 225 \times 13.6 \times 10^{-4}$ cm. The a- and b-axes, both 3.747 Å, point along the square diagonals, and the c-axis, 6.226 Å, is perpendicular to the plate. As Mo$K\alpha$ radiation was used the linear absorption coefficient is 934 cm^{-1} (Ref.[7]). The A values in Tables 1 and 2 are all referred to the cell diagonal $a\sqrt{2}$ $(= b\sqrt{2}) = 5.298$ Å as projection axis, and the precession angle 30°. For this case the indices are written $(h'k'l)$ where $h' = h + k$, $k' = h - k$ and (hkl) are the indices for the original cell.

The influence of m^3, the number of volume elements used during the numerical integration, is shown in Table 1. It is evident from the table that the convergency with increasing m is much dependent on the magnitude of A. Compare for instance the reflections (407) and (603).

Table 1.

	Influence of m^3, the number of volume elements, on the integration.						Percentage of volume in X-ray shadow.	
	$A \times 10_4$ $m =$							
$(h'k'l)$	5	6	7	8	9	10	α	(see below)
(002)	445	471	480	483	484	484	47	
(004)	911	925	936	942	945	946	31	
(008)	1797	1812	1821	1825	1828	1830		
(203)	247	272	280	285	288	290	28	
(400)	616	638	650	659	670	680		
(401)	567	598	608	613	621	626		
(402)	451	482	494	497	498	499		
(403)	323	351	361	362	364	364	17	
(404)	215	243	254	257	258	258	43	
(405)	598	636	650	654	655	655	34	
(406)	1131	1153	1165	1170	1173	1174	15	
(407)	1528	1546	1557	1564	1569	1572		
(603)	184	209	222	234	244	251	38	
(314)	456	509	531	538	540	539	19	
(716)	1264	1288	1310	1327	1339	1347	12	

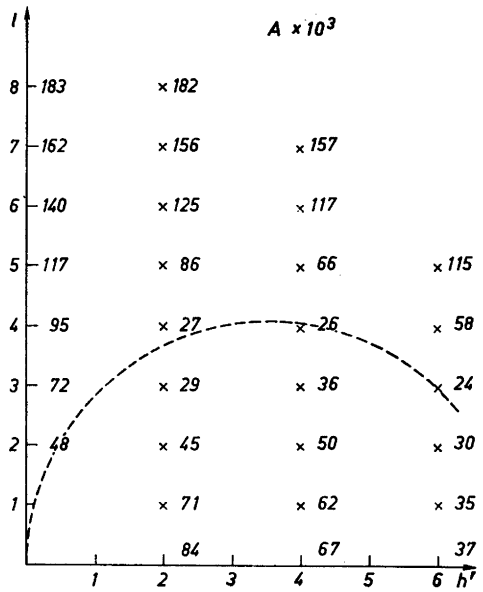

Fig. 1. Absorption factors in the zero level ($h'0l$). Maximum absorption around the semicircle.

α in Table 1 is the percentage of the volume elements which contribute less than $2.63 \times 10^{-4} \times m^{-3}$ each to the absorption factor. On account of a restriction in the standard routine for the exponential function these volume elements are omitted during the numerical integration. Approximately, we can say that α per cent of the crystal volume at most affects the fourth decimal in A. This indicates that the most important volume elements lie close to the surfaces, and for many reflections the deeper parts of the crystal lie in X-ray shadow. It may be noticed that the volume elements used during the integration process are smaller near the surfaces and bigger inside the crystal.[4,5] This should be an important advantage.

Fig. 1 shows the A values of the observed reflections in the zero level arranged in the same way as the spots occur on the film. The maximum absorption diagonals in Weissenberg photographs [8] correspond to semicircles on the reciprocal lattice.[9] It is convenient to use different m values and calculate some of the A values near this line before the final choice of m is made. In this case $m = 9$ was used.

The accuracy in A is naturally dependent on how accurately the shape of the crystal can be described. Let A_1 be the A for the crystal used, A_2 be the A for a plate where the thickness is reduced by 5 %, and A_3 be the A for a rectangular plate of the crystal obtained by reducing one of the other directions (which is much longer) by 5 %. Then the variations in the quotients A_1/A_2 and A_1/A_3 (*cf.* Table 2) show that it is necessary to determine the thickness of the plate very accurately. For an arbitrarily shaped crystal it may be stated that the most important measurement is the shortest way for the beam through the crystal. Therefore the necessity of good optical arrangements for the

Table 2. Influence of the measurement of the crystal and the μ value.

$(h'k'l)$	A_1/A_2	A_1/A_3	A_1/A_4
(002)	0.90	0.99	1.23
(007)	0.90	1.00	1.21
(008)	0.90	1.00	1.21
(400)	0.80	0.99	1.63
(404)	0.90	0.97	1.44
(600)	0.82	0.97	1.58
(314)	0.86	0.98	1.41
(716)	0.91	0.99	1.22

measurement of the crystal (in a coordinate system properly related to the axes of the unit cell) should be realized.[6]

Let A_4 be the A calculated with an old value of $\mu = 1144$ cm^{-1} (Ref.[10]). The importance of using an accurate value of μ is clearly shown in Table 2.

In order to show the influence of absorption errors, least-squares refinements[11] were made on the 35 observed $(h0l)$ reflections, corrected and uncorrected for absorption. The only parameters refined were the z coordinates for Bi and F and the calculated isotropic temperature factors for Bi, F, and O. The results are shown in Table 3 which may be compared with Table 2 in Ref.[1]

We may somewhat reduce the influence of absorption by taking averages of intensities measured on photographs taken with different projection axes. 76 reflections with the above mentioned cell diagonal and 106 reflections with a as projections axis were averaged. From this, 109 independent reflections (material B) were obtained. With these reflections, corrected and uncorrected for absorption, least-squares refinements were made.

Table 3. Atomic parameters, isotropic temperature factors and their standard deviations for the refinements of the structure BiOF.

Notation	R %	$z_{Bi} + \Delta z_{Bi}$	$B_{Bi} + \Delta B_{Bi}$	$B_O + \Delta B_O$	$z_F + \Delta z_F$	$B_F + \Delta B_F$
$(h0l)$ reflections uncorrected for absorption	31.1	0.2055 ± 0.0026	0.98 ± 0.31	−0.04 ± 2.47	0.674 ± 0.030	3.4 ± 2.6
$(h0l)$ reflections corrected for absorption	12.1	0.2065 ± 0.0009	1.22 ± 0.12	0.8 ± 1.9	0.667 ± 0.023	2.6 ± 2.6
Material B uncorrected for absorption	23.7	0.2062 ± 0.0012	1.14 ± 0.10	0.8 ± 1.8	0.683 ± 0.036	3.4 ± 2.6
Material B corrected for absorption *	10.1	0.2068 ± 0.0003	1.41 ± 0.03	0.5 ± 0.5	0.671 ± 0.009	2.9 ± 0.9

* These values are taken from Ref.[1]

The uncorrected (*h*0*l*) reflections give a very big *R* value and a "negative temperature factor" for the oxygen. In contrast to this we may notice that these 35 (*h*0*l*) reflections corrected for absorption give about the same parameters and standard deviations as all 109 reflections, averaged from 182, in the uncorrected material *B*. Furthermore the *R* value is about 50 % less. As expected the corrected material *B* gives the lowest *R* value and standard deviations. It is also seen in Table 3 that the absorption increases the standard deviations more than it changes the positions of the atoms. Finally it should be noticed that the *R* value seems to be even more sensitive for absorption errors than are the temperature factors.

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