

Table 2. Symmetry elements  $S_i$  and  ${}_jS$  for all possible types of space group rotations

Axis	Direction	$S_i$	${}_jS$
1		$(\pi + \theta_1, -\theta_2, \pi + \theta_3)$	$(\pi + \theta_1, -\theta_2, \pi + \theta_3)$
2	[010]	$(\pi - \theta_1, \pi + \theta_2, \theta_3)$	$(\theta_1, \pi + \theta_2, \pi - \theta_3)$
2	[001]	$(\pi + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi + \theta_3)$
4	[001]	$(-\pi/2 + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi/2 + \theta_3)$
3	[001]	$(-2\pi/3 + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, 2\pi/3 + \theta_3)$
6	[001]	$(-\pi/3 + \theta_1, \theta_2, \theta_3)$	$(\theta_1, \theta_2, \pi/3 + \theta_3)$
*2	[110]	$(3\pi/2 - \theta_1, \pi - \theta_2, \pi + \theta_3)$	$(\pi + \theta_1, \pi - \theta_2, -3\pi/2 - \theta_3)$

\* This axis is not unique (that is, it can always be generated by two other unique axes), but is included for completeness.

$$\begin{aligned}\cos \theta'_1 &= -\cos \theta'_2 \\ \sin \theta'_1 &= -\cos \theta_1 \sin \theta_2 / \sin \theta'_2 \\ \sin \theta'_3 &= (-\sin \theta_1 \cos \theta_2 \sin \theta_3 + \cos \theta_1 \cos \theta_3) / \sin \theta'_2 \\ \cos \theta'_3 &= (-\sin \theta_1 \cos \theta_2 \cos \theta_3 - \cos \theta_1 \sin \theta_3) / \sin \theta'_2 \\ \cos \theta'_2 &= \sin \theta_1 \sin \theta_2 \\ \sin \theta'_2 &= \pm [\sin^2 \theta_1 \cos^2 \theta_2 + \cos^2 \theta_1]^{1/2}.\end{aligned}$$

This is a threefold operation, in the sense that the application of this operation three times brings the original point back on itself. It is consistent with the infinite lattice in  $(\theta_1 \theta_2 \theta_3)$  space and can combine with other linear or non-linear operations to form a group,

although it cannot be described by one of the 230 space groups.

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## The Secondary Extinction Correction Applied to a Crystal of Arbitrary Shape

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Zachariasen's formula for the secondary-extinction correction has been successfully applied to a  $\text{BeAl}_2\text{O}_4$  crystal of irregular shape. An existing program for absorption correction of single-crystal diffraction data from arbitrarily shaped crystals could, after some minor modifications, be used for the necessary calculations.

The procedure used is described in some detail. It is shown that secondary-extinction errors can affect not only the vibrational parameters but also the positional parameters.

A re-examination of the Darwin formula for the secondary extinction correction (1922) was recently reported by Zachariasen (1963). It was shown that it contained an error in the X-ray diffraction case and a new formula was derived. This was tested on 'a perfect crystal sphere for which  $\mu r = 0.69$ '.

The expression for the corrected structure factor derived by Zachariasen is

$$F_{\text{corr}} \simeq F_o [1 + c \cdot I_o \cdot \beta(2\theta)] \quad (1)$$

where

$$\beta(2\theta) = \frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2} \cdot \frac{A^{*'}(2\theta)}{A^{*'}(0)}, \quad (2)$$

$F_o$  is the observed structure factor and  $F_{\text{corr}}$  is the former corrected for secondary extinction, both on the same scale.  $I_o$  is the uncorrected observed integrated intensity on an arbitrary scale, and  $c$  is a scale factor

to be adjusted.  $A^* = A^{-1}$  is the absorption factor for the reflexion and  $A^{*'}$  is  $dA^*/d\mu$ , where  $\mu$  is the linear absorption coefficient.

One of the present authors (Werner, 1964a, b) has constructed a program for the absorption correction of X-ray data from single crystals of arbitrary shape. It was found possible to make a slight change in the program so that the derivative  $A^{*'}$ , required in Zachariasen's formula, could be computed. Hitherto this change has been made only for the particular version of the absorption program handling single-crystal diffractometer data. The expression computed is

$$A^{*' = \frac{\sum_1^{m^3} \frac{1}{V_o} (r_\alpha + r_\beta) \cdot \exp [-(r_\alpha + r_\beta)\mu] \cdot \Delta V}{\left[ \sum_1^{m^3} \frac{1}{V_o} \cdot \exp [-(r_\alpha + r_\beta)\mu] \cdot \Delta V \right]^2} \quad (3)$$

where  $V_0$  is the volume of the crystal,  $r_a$  is the path length along the primary beam direction,  $r_b$  that along the diffracted beam direction,  $\Delta V$  the corresponding volume element and  $m^3$  is the number of volume elements. The  $\Delta V$ 's are selected in accordance with Gauss's numerical integration method (Margenau & Murphy, 1956). It should be pointed out that the computing time increases very little if  $A^*$  is calculated together with  $A$ .

The program forms one part of an integrated set of programs, written for data reduction of X-ray intensities obtained with the General Electric single-crystal diffractometer. The other members of this program series have been written by R. Norrestam at this Institute. Further details concerning the programs are given in a document (Norrestam, 1964), copies of which may be obtained from this Institute. All the programs are made for the computer Facit EDB.

In connection with a least-squares refinement of the crystal structure of chrysoberyl,  $\text{BeAl}_2\text{O}_4$ , using data obtained with a G.E. Single Crystal Orienter (Åsbrink, 1966), it was found that the measured intensities must contain some extinction errors. In fact, using absorption corrected three-dimensional data registered with Mo  $K\alpha$  radiation and  $2\theta \lesssim 100^\circ$ , it was found impossible to reach an  $R$  value less than 0.095. The number

of independent reflexions observed was 1225, but because of weakness 135 of them were considered somewhat uncertain and were not included in these calculations. The standard deviations of the 18 parameters including one scale factor remained unreasonably high and the 'temperature factors' were very low or even negative as can be seen from Table 1 (first rows). At this stage of the refinement, an investigation of the structure factors showed that for most of the very strongest reflexions the observed structure factor was numerically less than the corresponding calculated one (*cf.* Table 2a).

The strongest reflexions were then excluded in a stepwise manner, *i.e.* an increasing number of strong reflexions were left out in the continued refinement. That structure factor material was considered satisfactory for which a further exclusion of strongest reflexions in the next few least-squares cycles did not result in any systematic changes in the  $\Delta$ 's of the strongest of the remaining ones,  $\Delta$  being defined as  $|F_o| - |F_c|$ . The reduced material contained 88.3% of the data used from the start, *i.e.* 127 reflexions or about all with  $|F_o| \gtrsim 20$  were excluded. This smaller material was refined to an  $R$  value of 0.036. The resulting standard deviations of the positional parameters were only about 15% of their former values (*cf.* Table 1, second rows).

Table 1. Some data regarding  $\text{BeAl}_2\text{O}_4$  and the least-squares refinement of the structure

Space group:  $Pnma$  (No. 62)  
 Unit-cell dimensions:  
 $a = 9.4079 \pm 0.0010$ ,  $b = 5.4782 \pm 0.0006$ ,  $c = 4.4278 \pm 0.0005$  Å.  
 Cell content: 4  $\text{BeAl}_2\text{O}_4$ .  
 4 Al in 4(a):  $(0, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$   
 4 Al, 8 O and 4 Be in  $4 \times 4(c)$ :  $\pm(x, \frac{1}{4}, z; \frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$   
 8 O in 8(d):  $\pm(x, z, y; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z; x, \frac{1}{2}-y, z; \frac{1}{2}+x, y, \frac{1}{2}-z)$

Results from different stages of the refinement procedure using a block diagonal least-squares program for the computer Facit EDB (Åsbrink & Brändén, 1962).

First row for each atom: Only the 135 weakest reflexions omitted.  $R = 0.095$ .

Second row for each atom: The 135 weakest and the 127 strongest reflexions omitted.  $R = 0.036$ .

Third row for each atom: All 1225 reflexions, corrected for secondary extinction, used.  $R = 0.033$ .

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$
Al(1)	0	0	0	-0.098 ± 0.018 0.251 ± 0.003 0.257 ± 0.003
Al(2)	0.27324 ± 0.00019 0.27292 ± 0.00003 0.27292 ± 0.00003	$\frac{1}{4}$	0.99454 ± 0.00057 0.99488 ± 0.00006 0.99491 ± 0.00006	-0.135 ± 0.018 0.223 ± 0.003 0.229 ± 0.002
O(3)	0.09034 ± 0.00045 0.09022 ± 0.00006 0.09019 ± 0.00006	$\frac{1}{4}$	0.79001 ± 0.00099 0.78785 ± 0.00013 0.78788 ± 0.00013	-0.013 ± 0.044 0.234 ± 0.005 0.240 ± 0.005
O(4)	0.43472 ± 0.00044 0.43307 ± 0.00006 0.43308 ± 0.00006	$\frac{1}{4}$	0.24188 ± 0.00109 0.24192 ± 0.00014 0.24192 ± 0.00014	0.053 ± 0.045 0.260 ± 0.005 0.267 ± 0.005
O(5)	0.16261 ± 0.00030 0.16313 ± 0.00004 0.16314 ± 0.00004	0.01840 ± 0.00054 0.01529 ± 0.00007 0.01515 ± 0.00007	0.25662 ± 0.00073 0.25690 ± 0.00010 0.25687 ± 0.00010	0.049 ± 0.029 0.263 ± 0.003 0.271 ± 0.003
Be(6)	0.09267 ± 0.00096 0.09257 ± 0.00014 0.09258 ± 0.00013	$\frac{1}{4}$	0.43030 ± 0.00198 0.43355 ± 0.00027 0.43349 ± 0.00026	0.039 ± 0.095 0.355 ± 0.011 0.358 ± 0.011

Table 2. Comparisons between  $|F_o|$  and  $|F_c|$  for the 25 reflexions excluded in the second step of the refinement procedure (see text).

- (a) After refinement using all reflexions except the 135 weakest.  $R=0.095$ .  
 (b) After refinement where the 135 weakest and the 127 strongest reflexions were omitted.  $R=0.036$ . The change in  $|F_o|$  is explained by the more reliable scale factor obtained from the material where the reflexions most strongly affected by secondary extinction have been omitted.  
 (c) After refinement using the complete material corrected for secondary extinction.  $R=0.033$ .

<i>h k l</i>	(a)		(b)		(c)	
	$ F_o $	$ F_c $	$ F_o $	$ F_c $	$ F_o $	$ F_c $
0 4 0	93.4	113.6	75.6	111.5	110.7	111.4
0 8 0	56.0	55.7	45.3	49.5	48.8	49.4
6 2 0	88.8	100.6	71.9	99.0	102.5	98.9
6 6 0	60.5	57.9	49.0	53.6	54.1	53.4
1 0 1	32.9	30.7	26.6	31.2	31.8	31.2
1 1 1	39.8	37.5	32.3	38.4	39.6	38.4
1 2 1	43.4	41.5	35.2	42.3	41.6	42.3
3 0 1	49.8	53.6	40.3	54.8	51.2	54.7
4 0 1	59.4	65.2	48.1	64.7	62.9	64.7
5 2 1	49.8	47.3	40.4	45.3	46.1	45.3
7 0 1	54.2	53.6	43.9	51.1	50.4	51.1
2 2 2	78.2	90.2	63.3	88.7	90.0	88.6
2 6 2	51.2	50.1	41.5	45.9	44.7	45.8
4 0 2	71.5	82.9	57.9	81.7	77.8	81.7
4 4 2	59.4	58.0	48.1	55.4	54.8	55.3
8 0 2	52.8	49.9	42.7	47.9	47.5	47.8
1 2 3	43.1	40.4	34.9	38.8	38.2	38.8
2 2 3	46.1	42.3	37.4	41.7	41.3	41.6
3 0 3	41.8	39.9	33.9	38.0	37.0	37.9
4 0 3	43.1	39.2	34.9	38.9	38.1	38.9
7 0 3	49.9	48.0	40.4	44.8	44.2	44.7
0 0 4	82.8	84.9	67.1	82.1	87.9	82.0
0 4 4	64.8	65.0	52.5	60.8	59.8	60.7
6 2 4	58.5	56.8	47.3	53.6	52.7	53.4
2 2 6	43.4	42.6	35.2	37.3	37.0	37.2

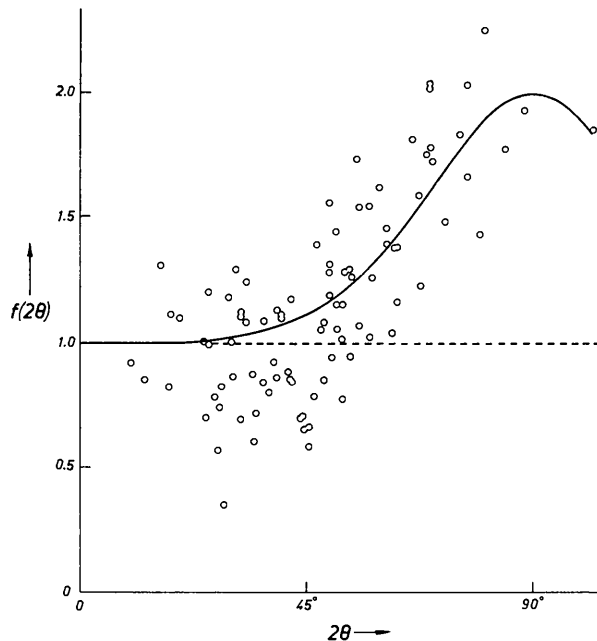


Fig. 1. Experimental values of  $f(2\theta)$  obtained with a crystal of chrysoberyl described by 10 plane surfaces. The full curve is the theoretical one calculated from equation (5). The dashed curve is according to Darwin.

Furthermore, all the  $B$  values had increased to a more satisfactory level. A renewed investigation of the structure factors of the excluded strong reflexions showed that the above-mentioned tendency was strengthened. (i.e. the  $A$ 's for the strongest reflexions had become more negative.) (cf. Table 2a and b.) From Table 2(a) it can be seen that for most of the reflexions presented the extinction error was very well masked when no strong reflexions were excluded in the refinement procedure. This is even more true for the about 100 somewhat weaker 'extinction reflexions' not included in Table 2.

At this point it was found worth while to apply secondary extinction corrections according to the procedure described above. Equations (1) and (2) were rearranged to

$$\frac{[|F_{\text{corr}}| - |F_o|] A^{*'}(0)}{c \cdot |F_o| \cdot I_o \cdot A^{*'}(2\theta)} = f(2\theta) \quad (4)$$

where

$$f(2\theta) = \frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2} \quad (5)$$

The function  $f(2\theta)$ , which does not depend on the actual crystal, is drawn in Fig. 1. (According to the Darwin formula the function  $f(2\theta)$  should have a constant value independent of  $2\theta$ .) In order to adjust the left hand side of equation (4) to a best fit to this theoretical function, the factor  $c$  had to be determined. This was done by the method of least squares, using the 94 strongest in the group of excluded reflexions and equating  $|F_{\text{corr}}|$  to  $|F_c|$  for each of them. Preliminary tests showed that errors in the remaining 33 weakest reflexions of the group had too much influence on the numerators in equation (4). The value obtained for  $c$  was  $(2.73 \pm 0.06) \cdot 10^{-5}$  with  $I_o$  on an absolute scale.

In Fig. 1 the left hand sides of equation (4) for these reflexions are plotted against  $2\theta$ . The agreement between the plotted points and the curve is fairly satisfactory (cf. Zachariassen 1963, p. 1143). It should be mentioned that the crystal used was of a rather irregular shape. For the calculations of the  $A$  and  $A^{*'}$  values the crystal was described by 10 plane surfaces. A  $\mu\bar{r}$  value  $\sim 0.07$  could be given it.  $A^{*'}(0)$  which is  $A^{*'}$  for an undeviated beam with the crystal in reflecting position is a function of the shape and orientation of the crystal. Therefore this function must be calculated for each reflexion if the crystal is not a sphere but of arbitrary shape.

Finally, secondary extinction corrections were applied to all the 1225 observed reflexions, whereupon 10 cycles of least-squares refinement were performed. In spite of the introduction of the formerly excluded 135 very weak reflexions (see above), the  $R$  value now decreased to 0.033. The parameters obtained are given in Table 1 (third rows). In Table 2(c) a comparison is made between the final  $|F_c|$ 's and the corrected  $|F_o|$ 's for the 25 reflexions left out in the second step of the above mentioned exclusion procedure.

### Discussion

When examining Table 1, one can see that besides the mentioned improvement of 'temperature factors' and standard deviations, in a few cases rather large changes appeared in the positional parameters when the influence of the secondary extinction errors was depressed. See for example the oxygen parameters  $z_3$ ,  $x_4$  and  $y_5$ . Thus the secondary extinction evidently may cause errors even in the positional parameters of the atoms in a crystal structure although it most strongly affects the vibrational parameters and scale factors. This example also shows that standard deviations cannot be trusted when large systematic errors are not corrected in the data. The rows 2 and 3 in Table 1 are in excellent agreement, which indicates that the secondary extinction corrections are correctly applied. The result thus speaks in favour of the Zachariassen formula.

Further information concerning the refinement and the detailed structure will be given elsewhere (Åsbrink, 1966).

### General conclusions

Secondary extinction errors could be appreciable and well worth the correction work. Mainly for two reasons, this has not been done very often. Firstly, because the quality of the intensity data used generally has not been sufficiently good. However, the advent of the modern single-crystal diffractometer has made possible the gathering of intensity data for which the statistical errors are depressed to a large extent so that the systematic errors play a more important role. Secondly, because of the laborious computational work involved.

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## The Yttrium Oxide – Titanium Dioxide System

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By means of X-ray powder photographs, it is shown that between 29 and 42 mol. % of yttrium oxide a solid solution having a pyrochlore structure exists, while between 46 and 61 mol. % a fluorite-type phase occurs. Between 42 and 46 mol. % there is a two-phase region. The phase change mechanism is discussed.

### Introduction

'Anomalous' solid solutions with a fluorite-type structure have been found between many oxides of the types

However, owing to the possibility of changing existing absorption programs for electronic computers, the work should not be unreasonable. Lastly, it should be pointed out that if the  $B$  values are to be considered as temperature factors and calculated electron densities relied upon as such, it is necessary to take all sources of error into account.

We wish to express our sincere gratitude to Prof. Arne Magnéli for his kind interest in the present work and for suggesting this paper. We are also indebted to Dr Rolf Norrestam for placing his diffractometer programs at our disposal. Thanks are also due to the Computer Division of the National Swedish Rationalization Agency for the use of the computers BESK and FACIT EDB. This investigation forms a part of a research programme financially supported by Malmfonden – Swedish Foundation for Scientific Research and Industrial Development.

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$M_2O_3$  and  $MO_2$  (Zintl & Croatto, 1939; Zintl & Udgard, 1939; Hund, 1951a, b; Hund, Peetz & Kottenhahn, 1955). These mixed oxides contain a fully occupied and undistorted cation lattice with random vacancies in the anion lattice. Yttrium oxide,  $Y_2O_3$ , and titanium dioxide,  $TiO_2$ , might be expected to form a similar solid solution, although the quadrivalent titan-