carried out on the Glasgow University KDF9 computer. Programs made available by D. McGregor, K. W. Muir, R. Pollard and Dr J. G. Sime were used in the Fourier refinement. The least-squares program was devised by Professor D. W. J. Cruickshank and J. G. F. Smith and the rigid-body thermal vibration analysis program by Dr W. S. McDonald and K. W. Muir. We are grateful to the referee for useful comments.

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Inclusion of secondary extinction in least-squares calculations*.

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A procedure for including secondary extinction as a parameter in crystal structure least-squares analysis is described and the effect of its use on the data for chrysoberyl is given.

Several years ago at this laboratory we began including the secondary extinction as a parameter in our least-squares refinements of crystal structure models. Several papers have now been published in which the results of such calculations have been included, as well as the equations used to define the least-squares model (*e.g.* Cromer, Larson & Roof, 1964). It is the purpose of this note to call attention to the technique and to present in support of its use some results on the refinement of chrysoberyl (Åsbrink & Werner, 1966), the data for which are quite strongly affected by extinction.

Common practice when severe extinction is evident is to omit the more greatly affected data from the final refinement. It is obviously undesirable, however, to remove the stronger and more heavily weighted data points. Less commonly the observed data are corrected by such methods as those of Hamilton (1957) or Zachariasen (1963). Correcting the observed data convolutes those data with a crystal 'parameter' which is most easily determined after the structure is known. Furthermore, the observed data published in a paper should be given as observed, not as corrected by some function which is a parameter of the crystal.

Starting with equation (13) of Zachariasen's (1963) paper and using his notation,

$$R/I_0 \approx R_0/I_0(1-\alpha R_0/I_0)\,. \qquad (1)$$

Substituting for R/I_0 and R_0/I_0 one obtains

$$F_o^2 \approx F_c^2(1-g\beta F_c^2)\,, \qquad (2)$$

where

$$\beta = \left(\frac{e^2N}{mc^2}\right)^2 \frac{p_2}{p_1}\,\frac{A\,dA^*/d\mu}{\sin 2\theta}\,.$$

Three approximations for the application of (2) to least-squares calculation will be described along with the derivatives needed. Results of tests on chrysoberyl (Åsbrink & Werner, 1966) are given below. The least-squares calculations were carried out by minimizing the quantity $\Sigma w(F_o-F_c^*)^2$, with

$$F_c^* = KF_c[1+g\beta(2\theta)F_c^2]^{-\frac{1}{4}} \qquad (3)$$

$$F_c^* = KF_c[1-g\beta(2\theta)F_c^2] \qquad (4)$$

and

$$F_c^* = KF_c[1-g\beta(2\theta)F_c^2]^{\frac{1}{4}}\,, \qquad (5)$$

where g is the secondary extinction parameter, K is a scale factor, and

$$\beta(2\theta) = \frac{p_2}{p_1}\,\frac{A\,dA^*/d\mu}{\sin 2\theta}\,. \qquad (6)$$

Equation (3)

Use of equation (3) is tantamount to assuming that the higher order terms of Zachariasen's (1963) equation (9), which were neglected in equation (2), are equal to $(-g\beta F_c^2)^n$, a fairly reasonable assumption.

The derivatives of F_c^* are

$$\frac{\partial F_c^*}{\partial \xi_i} = \left(\frac{\partial F_c}{\partial \xi_i}\right) K\,[1+g\beta(2\theta)F_c^2]^{-3/2} \qquad (7)$$

$$\frac{\partial F_c^*}{\partial K} = F_c\,[1+g\beta(2\theta)F_c^2]^{-\frac{1}{4}} \qquad (8)$$

* Work performed under the auspices of the U.S. Atomic Energy Commission.

Table 1. *Final values of parameters in chrysoberyl*

The x, y, and z values are $\times 10^5$ and the B values are $\times 10^3$. The numbers in parentheses are the standard deviation of the last figure listed.

		Å&W. No extinction	Larson. No extinction	Å&W. With extinction	$F_c^*=KF_c(1+g\beta F_c^2)^{-\frac{1}{4}}$	$F_c^*=KF_c(1-g\beta F_c^2)$	$F_c^*=KF_c(1-g\beta F_c^2)^{\frac{1}{4}}$
Be	x	9267 (96)	9239 (89)	9258 (13)	9273 (21)	9258 (28)	9251 (31)
	z	43030 (198)	43064 (180)	43349 (26)	43221 (42)	43110 (55)	43084 (61)
	B	39 (95)	60 (89)	358 (11)	345 (21)	260 (28)	238 (31)
Al(1)	B	−98 (18)	−112 (20)	257 (3)	189 (6)	137 (7)	120 (8)
Al(2)	x	27324 (19)	27320 (18)	27292 (3)	27291 (4)	27287 (6)	27288 (6)
	z	99454 (57)	99446 (53)	99491 (6)	99474 (12)	99469 (17)	99468 (19)
	B	−135 (18)	−154 (20)	229 (2)	141 (5)	85 (7)	67 (8)
O(1)	x	9034 (45)	9052 (43)	9019 (6)	9032 (10)	9034 (13)	9037 (15)
	z	79001 (99)	79050 (94)	78788 (13)	78844 (22)	78916 (29)	78936 (32)
	B	−13 (44)	−15 (42)	240 (5)	225 (10)	177 (14)	163 (15)
O(2)	x	43472 (44)	43458 (41)	43308 (6)	4331 (9)	43359 (12)	43368 (14)
	z	24188 (109)	24154 (102)	24192 (14)	24189 (23)	24157 (31)	24150 (34)
	B	53 (45)	49 (44)	267 (5)	259 (10)	216 (14)	204 (16)
O(3)	x	16261 (30)	16273 (28)	16314 (4)	16302 (6)	16296 (8)	16293 (9)
	y	1840 (54)	1806 (51)	1515 (7)	1570 (11)	1588 (16)	1595 (17)
	z	25662 (73)	25676 (68)	25687 (10)	25695 (16)	25692 (21)	25693 (23)
	B	49 (29)	45 (29)	271 (3)	257 (7)	211 (10)	197 (11)
Scale	$\times 10^3$	1000 (?)	1020 (5)	1000 (?)	833 (2)	867 (2)	878 (2)
g	$\times 10^6$	0	0	27·3 (6)	55·0 (6)	14·4 (1)	23·8 (2)
R	%	9·5	9·99	3·3	3·72	4·53	4·84
R_H		?	10·48	?	2·71	3·69	4·06
$\Sigma w(\Delta F)^2$		?	468·9	?	26·9	51·2	62·5

$$\frac{\partial F_c^*}{\partial g} = -\tfrac{1}{2}\beta(2\theta)KF_c^3[1+g\beta(2\theta)F_c^2]^{-3/2}, \qquad (9)$$

where the ξ_i are the positional and thermal parameters of the structure.

Equation (4)

Use of equation (4) assumes that the quadratic terms are equal to $\frac{1}{4}g^2\beta^2F_c^4$. Equation (4) is the F_c analog of Zachariasen's (1963) equation (14) which Åsbrink & Werner (1966) used on chrysoberyl. The value of g obtained with equation (4) is theoretically approximately half of that obtained with (3).

The equations for the derivatives of F_c^* are

$$\frac{\partial F_c^*}{\partial \xi_i} = \left(\frac{\partial F_c}{\partial \xi_i}\right) K[1-3g\beta(2\theta)F_c^2] \qquad (10)$$

$$\frac{\partial F_c^*}{\partial K} = F_c[1-g\beta(2\theta)F_c^2] \qquad (11)$$

$$\frac{\partial F_c^*}{\partial g} = -K\beta(2\theta)F_c^3. \qquad (12)$$

Equation (5)

Use of equation (5) is equivalent to assuming that the quadratic terms are zero, a rather poor assumption. For this equation the derivatives have the following forms:

$$\frac{\partial F_c^*}{\partial \xi_i} = \left(\frac{\partial F_c}{\partial \xi_i}\right) K\left(\frac{1-2g\beta(2\theta)F_c^2}{(1-g\beta(2\theta)F_c^2)^{\frac{1}{4}}}\right) \qquad (13)$$

$$\frac{\partial F_c^*}{\partial K} = F_c[1-g\beta(2\theta)F_c^2]^{\frac{1}{4}} \qquad (14)$$

$$\frac{\partial F_c^*}{\partial g} = \frac{-K\beta(2\theta)F_c^3}{2[1-g\beta(2\theta)F_c^2]^{\frac{1}{4}}} \qquad (15)$$

Discussion

The final values obtained for all the variables in the chrysoberyl structure by using each of the equations (3), (4) and (5) are given in Table 1 along with Åsbrink & Werner's (Å & W) values. In these calculations the term $AdA^*/d\mu$ was assumed to be constant and equal to 1·0. The form factors used in the calculations are those for the neutral species as given in *International Tables for X-ray Crystallography*, Vol. III. The weighting scheme was based on counting statistics and is that used by Åsbrink & Werner (1966). The full matrix was used in the least-squares calculation; Åsbrink & Werner had used a block-diagonal procedure. The discrepancies between the two sets of results uncorrected for extinction arise in part from Åsbrink & Werner's omission of the 135 weakest reflections in their calculations.

Hamilton (1964) has given a good procedure for evaluating the various sets of results. The ratio of R_H for equation (4) to equation (3) $[R_H=(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}}]$ is 1·22 and that for equation (5) to equation (3) is 1·30. The value of $\mathbf{R}_{18,1200,0\cdot005}$ is ~1·02. On this basis one determines that, at least for chrysoberyl, equation (3) provides the most satisfactory description of the secondary extinction parameter. This is the form of the extinction parameter which has been in use at Los Alamos for about 4 years, with the exception that before 1967 the terms involving the absorption had been neglected.

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