

is greater than the correct setting – a displacement of 2 mm is usually adequate. The doubling can be determined from curves given by Zoltai (1963). The method is most applicable to upper-level photography, because of the relatively longer exposure times needed. The exposure time for the pack of films must of course be doubled, as with the Zoltai screen, but a saving of time is achieved because up to six films can be exposed simultaneously.

The method has one further possible advantage – because the cassette is displaced away from the crystal for upper-

level photography, the value of ζ which can be recorded, before mechanical fouling of the cassette and the camera occurs, is increased slightly and thus in certain cases one higher level than normal can be recorded.

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The effect of absorption errors in a crystal structure refinement. By R. C. SRIVASTAVA and E. C. LINGAFELTER, *Department of Chemistry, University of Washington, Seattle, Washington 98105, U.S.A.*

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Because of the widely divergent opinions held by crystallographers on the subject of the extent to which failure to correct for absorption effects causes errors in both position and thermal parameters, we have carried out a series of calculations designed to investigate the question empirically. We have selected as a test compound bisethylenediamine-palladium(II) chloride, whose structure has recently been determined in this laboratory (Wiesner & Lingafelter, 1966). It contains one molecule of $\text{Pd}(\text{C}_2\text{N}_2\text{H}_8)_2\text{Cl}_2$ in a triclinic cell ($P\bar{1}$) of dimensions $a_0 = 6.878$, $b_0 = 8.325$, $c_0 = 4.980$ Å, $\alpha = 95^\circ 44'$, $\beta = 101^\circ 25'$, $\gamma = 108^\circ 52'$ ($\mu = 191$ cm $^{-1}$ for Cu $K\alpha$ radiation). Using the final atomic positions and a set of reasonable isotropic thermal parameters, we have

calculated a set of structure factors corresponding to 97% of the Cu $K\alpha$ sphere. For each member of a series of assumed crystal shapes we then calculated the absorption effect for Cu $K\alpha$ radiation for each reflection and applied this effect to the calculated structure factor, in this manner arriving at a set of hypothetical 'observed' structure factors uncorrected for absorption. The absorption effect has been calculated for diffractometer geometry assuming the crystal to be mounted about the c axis on an Eulerian cradle, and intensities to be collected with the plane of the χ axis normal to the plane of the ω and 2θ axes and bisecting the angle between the incident and diffracted beams. These hypothetical F_o 's have then been used to carry out full-

Table 1. *Parameter changes with estimated standard deviations in parentheses*

		Thermal parameter changes and e.s.d. $\times 10^2$						
		Positional parameter changes and e.s.d. $\times 10$						
Atom		I α , IV α	I ω	II α	II ω	III α	III ω	IV ω
Pd	<i>B</i>	-29 (1)	-2 (3)	-92 (2)	-57 (4)	-47 (3)	-5 (9)	-215 (4)
Cl	<i>x</i>	-5 (23)	-8 (53)	-4 (43)	-12 (87)	-15 (59)	-36 (177)	3 (83)
	<i>y</i>	1 (19)	1 (43)	3 (35)	1 (71)	-2 (48)	2 (144)	11 (67)
	<i>z</i>	1 (30)	-3 (70)	7 (57)	-8 (114)	-7 (78)	30 (232)	10 (109)
	<i>B</i>	-30 (3)	-2 (6)	-93 (5)	-56 (9)	48 (6)	-5 (19)	-2.17 (9)
N(1)	<i>x</i>	-23 (73)	-87 (168)	115 (137)	-119 (277)	-96 (193)	369 (538)	-21 (268)
	<i>y</i>	-60 (60)	-81 (136)	-12 (112)	45 (225)	-346 (157)	-840 (438)	176 (218)
	<i>z</i>	21 (97)	99 (220)	-70 (180)	-18 (363)	253 (252)	300 (705)	-88 (351)
	<i>B</i>	-23 (8)	5 (18)	-88 (14)	-49 (28)	-29 (20)	-16 (56)	-214 (25)
N(2)	<i>x</i>	93 (72)	80 (161)	65 (134)	113 (262)	124 (183)	282 (535)	-59 (262)
	<i>y</i>	-14 (58)	2 (131)	-85 (109)	-48 (213)	53 (149)	115 (436)	-315 (212)
	<i>z</i>	95 (94)	223 (211)	91 (176)	172 (343)	-439 (239)	-1063 (702)	371 (341)
	<i>B</i>	-31 (7)	-8 (17)	-92 (13)	-70 (26)	-48 (19)	-10 (56)	-217 (24)
C(1)	<i>x</i>	89 (100)	-9 (224)	231 (186)	-275 (369)	-223 (260)	106 (851)	-364 (364)
	<i>y</i>	-16 (81)	82 (182)	-93 (151)	73 (300)	88 (212)	590 (692)	-89 (296)
	<i>z</i>	186 (130)	161 (293)	240 (244)	441 (483)	471 (341)	3165 (1115)	11 (476)
	<i>B</i>	-29 (10)	-6 (24)	-93 (19)	-63 (37)	-35 (27)	+78 (93)	-219 (34)
C(2)	<i>x</i>	-9 (99)	18 (225)	-10 (186)	36 (371)	-64 (255)	154 (764)	98 (365)
	<i>y</i>	21 (81)	54 (183)	-8 (152)	93 (302)	22 (208)	234 (623)	-72 (299)
	<i>z</i>	9 (131)	55 (295)	-48 (245)	45 (487)	101 (355)	753 (1004)	-140 (481)
	<i>B</i>	-29 (10)	-4 (24)	-92 (19)	-60 (38)	-46 (26)	6 (81)	-217 (34)
<i>R</i>		0.036	0.081	0.066	0.135	0.087	0.290	0.134
<i>l</i> ₁ (mm)		0.064	0.064	0.127	0.127	0.064	0.064	0.510
<i>l</i> ₂ (mm)		0.078	0.078	0.157	0.157	0.157	1.411	0.470
<i>l</i> ₃ (mm)		0.098	1.947	0.122	1.951	0.122	1.463	0.488

matrix least-squares refinements of an overall scale factor and of positions and B 's for all atoms except hydrogen, using unit weight for all reflections. The quantity minimized was $\sum w(F_o - F_c)^2$. In each case the refinement was continued until the maximum shift of any parameter was less than one-half of the estimated standard deviation.

The crystals were assumed to be bounded by {100}, {010} and {001}. The perpendicular distance between each set of parallel and opposite faces (l_1, l_2, l_3) was varied in different cases so as to give rise to four shapes of crystal, needles of small cross-section (shape I), needles of medium cross-section (shape II), plates (shape III), and nearly regular parallelepipeds (shape IV).

The results of the calculations on the smallest (labelled α) and largest (labelled ω) crystal of each of the shapes are listed in Table 1. Examination of the table shows the following general effects:

(1) For a given crystal shape, the isotropic temperature factors of all atoms are changed by essentially the same amount. In five of the seven cases listed, the change in B is many times larger than the estimated standard deviations.

(2) In the case of regular parallelepipeds (shape IV), as one goes from smaller to larger crystals the ΔB 's, which are negative, increase in magnitude so much that, in crystal IV ω , B_{Pd} has become negative. Such a trend would be expected, since a particular set of F_o 's should show the average slope of the absorption correction line, and this would be related to the volume of the crystal. However, in the case of needles and plates, as one increases the length of the needle or the face area of the plate, ΔB becomes less negative. This is so because, in needles mounted about the needle axis, any increase in length affects a large number of high-angle reflections whereas most of the lower angle reflections are affected very little. This means a greater decrease in the intensity of a large number of high-angle re-

flections as compared with lower angle ones, which will show up in an increase of the B 's. The same kind of behaviour will be observed if the face area of a plate mounted about one of its edges is increased.

(3) Some of the positional parameter changes are quite large (the largest being 0.16 Å for z of C(1) in case III ω), but the estimated standard deviations are also large. Only seven of the 105 changes are $> \sigma$, only two are $> 2\sigma$, and none are $> 3\sigma$.

In another series of calculations we investigated the effect of introducing random errors into the set of F_o 's. Eight cases were studied. In every case, introduction of a set of normally distributed random errors (mean=0, $\sigma=5\%$) caused R to increase somewhat, σ to increase slightly or not at all, and the shifts to become quite different although of about the same average magnitude. In two cases anisotropic refinement was carried out and, as might be expected, R decreased. The shifts in positional parameters changed, but in general there was no significant change in their average magnitude. Thus it appears that a part of the absorption error was compensated by changes in the B_{ij} 's. Presumably one could correlate the changes in shape and size of the vibration ellipsoids of different atoms with the changes in shape and size of the crystals but we have made no such study.

After this study was completed, a similar conclusion has been reported by Werner (1964).

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Note on the nine-layer hexagonal structure of YAl_3 . By T. DAGERHAMN and S. WESTMAN, *Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden*

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In the yttrium-aluminum system there occurs a phase of the composition YAl_3 , reported to be rhombohedral, with hexagonal lattice parameters $a=6.195$, $c=21.17$ Å (Bruzzone & Ferro Ruggiero, 1962) or $a=6.194$, $c=21.138$ Å (van Vucht & Buschow, 1964). The latter authors assume the structure to be a nine-layer sequence to fit the c/a ratio.

The present investigation yields $a=6.195$, $c=21.129$ Å, $c/a=3.411$, from X-ray Guinier powder photograph data for an alloy prepared from components weighed out to correspond to the composition $YAl_{3.00}$. The weight loss in the arc-melting process of preparation was less than 1% of the Al content. The phase appears to be stoichiometric. The structural principle has been verified from Weissenberg intensity data, and a refinement has been carried out yielding the following results. Each layer has the composition YAl_3 , and the layer sequence is $\cdots ABABCBCAC \cdots$ or $\cdots chhchhchh \cdots$ to indicate whether the immediate surroundings are of the h.c.p. or the c.c.p. type.

The space group is $R\bar{3}m$ (No. 166) with 36 atoms per hexagonal unit cell.

$(0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}) +$

3 Y(1) in (a): 0, 0, 0

6 Y(2) in (c): 0, 0, z ; 0, 0, \bar{z} with $z=0.2180 \pm 0.0003$

9 Al(1) in (e): $\frac{1}{2}, 0, 0$; 0, $\frac{1}{2}, 0$; $\frac{1}{2}, \frac{1}{2}, 0$

18 Al(2) in (h): x, \bar{x}, z ; $x, 2x, z$; $2\bar{x}, \bar{x}, z$

\bar{x}, x, \bar{z} ; $\bar{x}, 2\bar{x}, \bar{z}$; $2x, x, \bar{z}$

with $x=0.4785 \pm 0.0006$ and $z=\frac{2}{3}$

The temperature factors are: $B(Y)=1.1 \pm 0.1$ Å² and $B(Al)=1.8 \pm 0.4$ Å². Some of the atomic positional parameters deviate significantly from the ideal values for close packing of equal spheres, that is $z_Y=2/9=0.2222$ and $x_{Al}=\frac{1}{2}$. The value of z_{Al} , however, remains unchanged within the accuracy of the refinement. This was carried out for 212 independent reflexions, using a least-squares program (Åsbrink & Brändén, 1962) available at this Institute. The program treats only orthorhombic and lower symmetries, and thus the errors computed for the structural parameters should not be taken as true standard deviations. Their