MATERIAL FOR DEPOSIT Revised 16 January, 2000.

HOW PRECISE ARE MEASUREMENTS OF UNIT CELL DIMENSIONS FROM SINGLE CRYSTALS?

Frank H. Herbstein, Department of Chemistry, Technion–1srael Institute of Technology, Haifa, Israel 32000 (e-mail: chr03fh@tx.technion.ac.il)

(Received ; accepted).

Synopsis: The best measurements of cell dimensions from (small) single crystals and powders on the most favourable specimens have a precision of some parts in 10^5, which seems to be the maximum attainable with current, and older, techniques. There has been little real improvement over a period of some sixty years. 'Routine' measurements, on less favourable specimens, give precisions of some parts in 10^4 or even 10^3. Some current assessments of the standard uncertainties of cell dimensions are fictional at best.

Abstract. The results of single-site and many-site measurements of cell dimensions from single crystals are compared for Bond and four-circle diffractometers using samples of corundum (essentially pure rhombohedral α-Al_2O_3) of high diffraction quality, where the effects of small changes in temperature and composition (Cr_2O_3 in solid solution) can be taken into account. Similar comparisons are made for four-circle diffractometer measurements on ruby (α-Al_2O_3 with 0.46 wt % Cr in solid solution). The precisions are some parts in 10^5. There is *partial* support for the Taylor-Kennard 1986 dictum (*Acta Cryst*. (1986), B**42**, 112–120) that standard uncertainties (s.u.s) of cell parameters from routine four-circle diffractometer measurements are less than those for many-site measurements by factors of 5 for cell lengths and 2.5 for cell angles. For organic crystals, independent repetitions of adequate quality for comparison and analysis of routine four-circle diffractometer measurements are available only for α-oxalic acid dihydrate and anthracene. The experimental standard uncertainties given for these two crystals agree reasonably well with the sample s.u.s at room temperature but appreciably less well at •100 K, again giving partial support to the Taylor-Kennard dictum. The relation between specimen characteristics and attainable precision is emphasized; the precisions for routine measurements on good quality organic crystals are some parts in 10^4. Area detector measurements of cell dimensions have also been appraised; currently published s.u.s from such measurements appear to be highly unreliable, and this is supported by a recent analysis of the operation of such diffractometers (Paciorek, Meyer & Chapuis, (1999), *Acta Cryst*. A**55**, 543–557)). Formulation of a standard protocol for such measurements is badly needed. The dangers inherent in high degrees of replication are illustrated by recounting Kapteyn's Parable of the Chinese Emperor. Attention is drawn to the fact that there has been little improvement in claimed precisions over the past forty to sixty years.

Table A1. Notes prepared by Dr. E.J. Gabe, (Chemistry Division, NRC, Ottawa, Canada, K1A 0R6) to accompany ruby-sphere memento distributed to participants in IUCr XII. Included with Dr Gabe's permission.

"SPHERICAL CRYSTALS USEFUL IN DIFFRACTOMETER ALIGNMENTS

The Organizing Committee of the XIIth Congress of the International Union of Crystallography has attempted to provide participants with a memento of the Congress which is both useful and has crystallographic significance. Accordingly, attached to this sheet there are two small single-crystal ruby spheres. We propose that these spheres be used for the alignment and set-up of diffraction equipment and the following information is provided for this purpose.

CAUTION: The two spheres are mounted between two pieces or tape, in the circle on the small card attached to this sheet. They are hard to see and EASY TO LOSE. The crystals can be recovered by piercing the tape with a needle and then soaking the mount in an organic solvent.

Ruby Sphere Data

Diameter	0.152±5 mm; sphericity 0.0013 mm
Composition	$A1_20_3$; Cr 0.46 $\pm$ 0.03% wt.
Mosaic spread	Very small
Space Group	R-3c
	Al in position 12c 0,0,z
	O in position 18e x,0,1/2

The following results were obtained from four ruby spheres chosen at random. The results for pure $A1_20_3$, obtained by the same methods, are quoted for comparison.

Cell Parameters

Least squares refinement of 2θ data on 74 reflections with 105° • 2θ • l20° , at 26.2 ± 0. 1°C with MoKα_1 radiation, λ = 0.70932 Å.

Sphere	1	2	3	4	Pure $A1_20_3$
a (Å)	4.76094(3)	4.76104(6}	4.76094(6)	4.76106(6)	4.75999(3)
c (Å)	12.99616(16)	12.99640(16)	12.99580(16)	12.99662(14)	12.99481(7)

Mean a = 4.76099(6) Å, mean c = 12.99625(35) Å.

Structural Parameters

Data collected with the θ/2θ scan technique at 4° / min and profile analysis applied. Graphite rnonochromatized MoKα_1 radiation derived from a tube operated at 50kV, 10 ma was used and $2\theta_{max}$ = 120°; (90° for $A1_2O_3$).

Sphere	1	2	3	4	Pure $A1_20_3$
Reflns.	880/414	886/415	1039/414	942/410	2844/217
<•I> / <I>	0.006	0.009	0.016	0.009	-
Al z	0.35227(2)	0.35229(3)	0.35225(2)	0.35226(2)	0.35219(1)
u_{11}	0.00312(8)	0.00309(9)	0.00306(8)	0.00300(9)	0.00338(5)

u_{33}	0.00355(10)	0.00361(11)	0.00343(10)	0.00349(11)	0.00335(5)
O x	0.69374(11)	0.69373(13)	0.69380(13)	0.69382(12)	0.69367(5)
u_{11}	0.00369(12)	0.00364(14)	0.00362(12)	0.00356(13)	0.00359(6)
u_{33}	0.00369(13)	0.00364(15)	0.00352(13)	0.00366(14)	0.00394(S)
u_{12}	0.00173(13)	0.00166(16)	0.00170(14)	0.00164(15)	0.00166(7)
u_{13}	0.00029(6)	0.00030(7)	0.00029(6)	0.00029(7)	0.00035(3)
Scale	0.2673(1)	0.2472(1)	0.2820(1)	0.2792(1)	0.1496(4)
Ext. (μm)	0.76(3)	0.32(2)	0.75(3)	0.66(3)	0.52(3)
R_F	0.0158	0.0178	0.0152	0.0162	0.0134
R_W	0.0257	0.0318	0.0262	0.0284	0.0068

For crystal 2 even though the extinction and scale parameters differ, the other parameters are
unaffected; the range of scale factors is consistent with the range of diameters.

The following reflections can be used for initial orientation of the spheres.

h k l	Fo	Multiplicity	$2\theta_{CuK\alpha_1}$	$2\theta_{MoK\alpha_1}$
006	14	2	41.66	18.85
0012	51	2	90.67	38.23
300	137	6	68.18	29.91

Accurate alignment can be carried out with the following intense high angle reflections

h	k	l	Mult	Fo	$2\theta_{CuK\alpha_1}$	h	k	1	Mult	Fo	$2\theta_{MoK\alpha_1}$
0	1	4	6	52	116.55	0	0	30	2	31	109.90
1	3	10	12	63	127.60	3	0	30	6	27	118.28
2	2	9	12	28	114.00	5	2	24	12	21	115.80
3	0	12	6	36	129.79	7	3	10	12	31	108.54
3	1	8	12	36	110.93	4	6	10	12	27	105.88
3	2	4	12	61	116.02	0	3	30	6	27	118.28
4	1	0	6	46	117.77	0	7	20	6	28	108.70
4	1	3	12	24	121.95	1	9	10	12	19	119.70

We feel that these spheres make excellent standard single crystals and recommend their use. There are many intense reflections with high multiplicities at high angles, with which diffractometers can be set up. We would appreciate it if cell and structure parameter results were sent to Dr. E.J. Gabe, Chemistry Division, NRC, Ottawa, Canada, K1A 0R6. If sufficient interest is generated the results will be published."

Table A2. Details of measurements on ruby spheres by Dr. E.J. Gabe, (Chemistry Division, NRC, Ottawa, Canada, K1A 0R6). Included with Dr Gabe's permission.

"We measured about 100 reflections with 2theta between 122 and 136 degrees, on 12 crystals with Cu radiation (wavelength 1.540560), on a CAD4 instrument usingthe control program DIFRAC. We repeated the measurements on 3 of the crystals to give us some idea of reproducibility.

No.	a (esd) Å	c (esd) Å	Nref	t(°C)	Comments
1	4.760516(51)	12.99457(15)	101	20.4	
2a	4.760128(65)	12.99392(17)	100	20.2	Lowest values
2b	4.760228(54)	12.99405(14)	100	20.3	Repeat of 2a
3	4.760434(63)	12.99424(17)	102	20.7	
4	4.760386(51)	12.99442(14)	103	20.2	
5a	4.760466(67)	12.99431(19)	98	22.6	
5b	4.760459(60)	12.99455(17)	101	22.6	Repeat of 5a
6a	4.760645(58)	12.99508(16)	98	19.5	Highest values
6b	4.760674(67)	12.99550(19)	98	21.0	Repeat of 6a
7	4.760422(58)	12.99469(16)	99	20.4	
8	4.760322(59)	12.99402(16)	99	19.2	
9	4.760356(54)	12.99428(15)	100	19.0	
10	4.760429(63)	12.99413(17)	100	20.0	
11	4.760487(74)	12.99398(23)	99	19.9	
12	4.760224(62)	12.99399(14)	100	19.9	

We repeated the measurements on crystal #5 (a and b) to check reproducibility and as you see it is satisfactory. At the end we noticed that the values from crystals 2 and 6 were the lowest and highest, so we repeated those as well and the results confirmed that those crystals did indeed give low and high values. The results also confirm that the precision of any single set is a little less than 1 part in 100,000 as anticipated; elaborate corrections which are smaller than this were not made. If we [somewhat arbitrarily] omit the outlier sets 2a, 2b, 6a and 6b, then we get mean values of a = 4.760408((25) Å and c 12.99432(7) Å.

Table B. Comparison of cell dimensions of corundum given by various authors. Temperatures of measurement are given for some values, while others have been corrected to 298.15 K, and this is noted.

Sample / T(K)	*a*(Å)	*c*(Å)	Methodology	Reference
corundum; 298.15	4.759288 (27)	12.991544 (242)	*c* from 00.12 (FeKα_1), then *a* from *c* and d(40.8) (Cu Kα_1); for both reflections, 2θ •126°; measured at 297.35 K.7	Cooper(1962)
corundum; 298.15	4.758956 (3)	12.994746 (70)	As for ruby below; Mo Kα_1; measured at 299 K.	Gabe (1981)

corundum; 293 K	4.7540(5)	12.9820(6)	Some (but incomplete) details given in paper; four-circle diffractometer (Mo Kα and synchrotron).	Maslen *et al*. (1993)
corundum	4.7586(1)	12.9897(1)	Debye-Scherrer, (λ • 1.4855 Å; synchrotron).	Thompson, Cox & Hastings (1987)
corundum	4.75855(2)	12.9906(1)	Polycrystalline flat plate (λ • 1.4855 Å; synchrotron).	Cox *et al*. (1981)
corundum	4.75893(1)	12.9917(7)	NIST SRM 674 (polycrystalline sample)	Table 5.2.11.1 of Parrish & Wilson (1995)
corundum	4.758548 (4)	12.9932(12)	Powder diffractometer, internal standard.	Steinwehr (1967)
corundum; 295 K	4.7570(5)	12.9877(35)	5-circle diffractometer (λ • 0.5591 Å; synchrotron).	Kirfel & Eichhorn, (1990)
corundum; 304 K	4.76307	13.008944	Debye-Scherrer and back reflection	Shinoda & Amano, (1950)
Ruby/298.15/ 0.5 mol % Cr_2O_3	4.760585 (144)	12.994637 (436)	four-circle diffractometer (Cu Kα)	Gabe (1981)
Ruby/298.15/ 0.5 mol % Cr_2O_3	4.760952 (64)	12.996181 (351)	four-circle diffractometer (Mo Kα)	Gabe (1981)
Ruby/ 0.5 mol % Cr_2O_3	4.76080 (29)	12.99568 (87)	four-circle diffractometer	Siegrist *et al*., (1999)
Ruby/ 0.5 mol % Cr_2O_3	4.76093 (31)	12.9959 (23)	Guinier camera	Siegrist *et al*., (1999)
Ruby/ 1.0 mol % Cr_2O_3	4.7597 (4)	13.0013 (9)	Position sensitive detector; (Cu Kα)	Estifanos *et al*., (1997)

Table C. Cell dimensions of rubies of various compositions as given various authors.

Author	mol fraction Cr_2O_3	a(Å)	c(Å)
Graham	0.008	4.7615	13.0000
Graham	0.014	4.7660	13.0090
Graham	0.02	4.7705	13.0230
Graham	0.032	4.7775	13.0380
Graham	0.05	4.7890	13.0650
Graham	0.07	4.8015	13.1000

Graham	0.109	4.8150	13.1350
JSD60	0.0009	4.7594	12.9902
JSD60	0.002	4.7595	12.9909
JSD60	0.0043	4.76025	12.9912
JSD60	0.0162	4.7633	12.9996
JSD60	0.0184	4.7638	12.9998
Cooper	0	4.75903	12.99086
Gabe	0.0045	4.76077	12.99541
Moss/Newnham	0.04	4.769	13.018
Efinamos	0.01	4.7597	13.0013
Shalnikova/Yakovlev	0	4.7593	12.9832
Shalnikova/Yakovlev	0.01	4.7586	12.9882
Shalnikova/Yakovlev	0.0195	4.7617	12.9932
Shalnikova/Yakovlev	0.0718	4.7739	13.0202