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How precise are measurements of unit-cell dimensions from single crystals?

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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, aluminum oxide) of high diffraction quality, where the effects of small changes in temperature and composition (Cr_2O_3, chromium oxide, 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 [*Acta Cryst.* (1986), B**42**, 112–120] dictum 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 $\sim$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 *et al.* (1999). *Acta Cryst.* A**55**, 543–557]. Formulation of a standard protocol for such measurements is badly needed. The dangers

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Frank H. Herbstein was born in Cape Town in 1926. He considers himself to be fortunate in his teachers – R. W. James at the University of Cape Town, G. M. J. Schmidt at the Weizmann Institute, B. E. Warren at MIT. After 9 years at the South African Council for Scientific and Industrial Research in Pretoria, he was appointed Professor of Chemistry at Technion in Haifa in 1965, where he has remained, filling a number of senior administrative positions and nominally retiring in 1994. He has also been fortunate in visiting appointments – at Caltech (leading to a longstanding fruitful collaboration with R. E. Marsh), Northwestern, Churchill College (Cambridge) and the Universities of Cape Town and the Witwatersrand. He was elected a Foreign Associate of the Royal Society of South Africa. Activities in the IUCr have included membership of the Apparatus and Structural Chemistry Commissions and stints as a Co-editor of Acta A, B and C. He has also chaired the Israel Crystallography Association a number of times.

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 40–60 years.

1. Introduction

Measurement of cell dimensions is an essential preliminary step in the determination of crystal structures and the values are basic to many other branches of crystallographic study. A very comprehensive account of modern methodology and techniques as applied to single crystals[1] is given by Galdecka (1995, revision in 1999), and for polycrystalline samples by Parrish & Wilson (1995; revision by Parrish *et al.*, 1999). How precise and accurate (see below for definitions) are such measurements as currently performed in crystal structure determinations, and how reliable are the estimates of their standard uncertainties (s.u.s)? I start with a critical survey of the more precise published results, especially for corundum and ruby, in order to establish optimum conditions, and what is attainable under these conditions, and then extend the discussion to the more routine level. The quality of the results is determined by an interaction between experimental methodology, including instrumentation, on the one hand, and the limitations imposed by the nature of the specimen, on the other. The skill of the experimenter, once so vital, seems to have lost importance in this Age of Automation.

One approach could be to carry out a round-robin set of single-crystal cell dimension measurements, preferably on a triclinic crystal of established purity, reproducibility and diffraction quality (or a crystal of higher symmetry but treated as triclinic). This method was used in the 'IUCr precision lattice parameter project' carried out approximately 40 years ago using diamond, tungsten and silicon powders (report by Parrish, 1960). A single-crystal analogue using ruby and zeolite samples is on the verge of completion. Progress was reported to the IUCr Executive Committee by the Commission on Crystallographic Apparatus in 1993 and 1996;[2] a poster summarizing later work was presented at the IUCr Glasgow Congress and General Assembly (Siegrist *et al.*, 1999). First steps towards answering the second part of the question posed above were taken by Taylor & Kennard (1986; TK86), who reported that 'the e.s.d's of cell parameters are grossly underestimated, by an average factor of about 5 for cell lengths and 2.5 for cell angles'. The TK86 assessment was made by comparing cell dimensions of (predominantly chance) duplicate structure determinations reported in the CSD (Allen *et al.*, 1991). There were 96 examples in the TK86 sample, all organic or organometallic molecular (single) crystals, and the measurements were made on a four-circle diffractometer using graphite-monochromated Mo $K\alpha$; the methodologies used by the various authors can be fairly described as 'routine'.

An improvement could be to compare multiple (not just duplicate) measurements on a particular crystalline material at a given temperature; here it would be desirable to segregate the groups of results according to the claimed precision of the measurement methodology. There are not many candidates for such an examination; in the present context 'multiple' is less than about 10. Rather precise room-temperature measurements have been made for corundum (essentially pure rhombohedral α-Al_2O_3; also called sapphire); here, the effects of small changes in temperature and composition (Cr_2O_3 in solid solution, giving rubies of various compositions) can be assessed from published results. Among organic crystals, using 'routine' techniques, multiple comparisons are warranted only for α-oxalic acid dihydrate and anthracene (both over a wide range of temperatures).[3]

2. Precision, accuracy and nomenclature

Not all books on statistics mention 'precision' and 'accuracy' in their indexes. Authoritative currently accepted definitions are given in 'Statistical Descriptors in Crystallography' (Schwarzenbach *et al.*, 1989) and 'Guidelines for Evaluating and Expressing the Uncertainty of *NIST* Measurement Results' (Taylor & Kuyatt, 1994). I follow here Schwarzenbach *et al.* (1989) who define 'precision' as 'the closeness of agreement between the values of a measurement or of an *estimate* obtained by applying a strictly identical experimental procedure several times'. 'Accuracy' is defined as 'the closeness of agreement between the value of an *estimate*, derived from a physical measurement, and the true value of the quantity (measurand) estimated'. This definition is followed by 'the reference to the true value implies that *in practice accuracy cannot be exactly evaluated*' (my italics). The experimenter is also warned that 'precise estimates are not necessarily accurate'. The differences between 'Descriptors' and 'Guidelines' are minor. I have avoided the use of the term 'accuracy' and instead compare the standard uncertainties of 'single-site'[4] and 'many-site' measurements. This is similar to the approach of Parrish & Wilson (1995; see pp. 427–428), who associate 'precision' with 'single-site' results, and (the here banished) 'accuracy' with 'multiple-site' results.

It is the policy of the IUCr to require all published numerical values to be accompanied by a standard uncertainty (s.u., defined below) 'expressed as a number in parentheses following the numerical result and should be on the scale of the least significant digits of the result' [for example, see Notes for Authors (1999). *J. Appl. Cryst.* **32**, 136–142, §8]. However, *which* s.u. is intended? – of an experimental measurement, of a

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[1] Measurements of cell dimensions for the large single crystals used in the semi-conductor industry are expressly excluded from discussion in this paper.

[2] I am grateful to Mr M. H. Dacombe, Executive Secretary, IUCr, for copies of these reports.

[3] I have considered naphthalene (deposited Table F), acetamide (deposited Table G) and potassium tetraoxalate dihydrate as candidates for inclusion, but rejected them because there are not enough data. Webster (1998) has given a wide-ranging summary of potential diffractometer test crystals.

[4] 'Site' is given a broader connotation than geographical. In a single-site set of measurements the conditions are kept fixed; in multiple-site measurements the conditions (specimen, instrument, wavelength) are varied from one set to the next.

Table 1
Some examples of high precision measurements (at room temperature) of cell dimensions (Å, °) of molecular crystals.

Compound	a	b	c	β	Reference
Sulfur	10.4646 (1)	12.8660 (1)	24.4860 (3)	–	†
(D)-(+)-Tartaric acid	7.7290 (1)	6.0004 (1)	6.2126 (1)	100.153 (1)	‡
Hexabromobenzene	15.3816 (10)	–	8.3768 (6)	92.691 (4)	§

† Sulfur at 297.8 (1) K; Bond method, using Cu $K\alpha_1$ and Co $K\alpha_1$ radiation (Cooper *et al.*, 1961; Cooper, 1962). ‡ (D)-(+)-Tartaric acid at 298 K; Bond method (A. S. Cooper, 1961, unpublished, quoted by Abrahams *et al.*, 1970). § Hexabromobenzene by back-reflection Weissenberg method (Herbstein, 1963; Cu $K\alpha_{1,2}$); b is not given as it was determined by another, less precise, method.

sample (or population) containing a number of numerical results, of the sample mean *etc.* A bracketed number is hardly able to give an adequate answer, and I have attempted to clarify my intentions by a suitable nomenclature. Cell dimensions 'y_i' (= a, b, c, α, β, γ) are derived from angle measurements of the reflections from a particular crystal using a diffractometer or camera; the number of reflections used differs from one experimental methodology to the next. The values of 'y_i' obtained from different reflections will differ, and $u_{\rm exp}(y_i)$ is the experimental standard uncertainty assigned (usually by 'black box' software) to their probability density function. It is the number that appears bracketed in a = 12.3456 (7) Å in most crystallographic publications; the s.u. is that given by the original investigators, unless stated otherwise. If this measurement has been repeated N times under the same conditions, then there is a single-site sample of N measurements (y_i, i = 1–N) of the cell dimension and its precision (in the sense defined above) is given by the standard uncertainty (for simplicity, weighting factors have been ignored)

$$u_{\rm sample}(y_i) = [(\Sigma(y_i - \langle y_i \rangle)^2)/(N-1)]^{1/2}, \qquad (1)$$

where the summation is over N observations. If the conditions remain unchanged from measurement to measurement, then $u_{\rm exp}(y_i) \simeq {\rm u}_{\rm sample}(y_i)$. Such tests are seldom made in crystal structure determination and it is usually assumed that $u_{\rm exp}(y_i)$ is an adequate measure of the single-site precision. It is more usual to have a many-site sample, where some parameter (*e.g.* diffractometer, crystal, wavelength) has been changed from one measurement to the next. I have noted in the text whether $u_{\rm sample}(y_i)$ is single-site or many-site; usually the many-site $u_{\rm sample}(y_i)$ has been calculated here from the published y_i. If the s.u. of the (generally many-site) sample mean $\langle y_i \rangle$ is required (possibly to define a standard value of a dimension), then

$$u_{\rm mean}(\langle y_i \rangle) = u_{\rm sample}(y_i)/(N)^{1/2}. \qquad (2)$$

It is often convenient to describe the quality of results more loosely as having a precision of some parts in 10^n, especially when comparing dimensions of different sizes.

There is one difference of detail between my approach and that of TK86. In their work (referring specifically to that part concerned with cell dimensions), TK86 determined the number of occurrences $N(\delta(y)_{ij})$ ['i' refers to the serial number (1–96) of the pair, 'j = 1–3' refers to the cell dimension, y symbolizes length or angle], where $\delta(y)_{ij} = \{(y_{ij1} - y_{ij2})/[u^2(y_{ij1}) + u^2(y_{ij2})]^{1/2}\}$, in their sample of 96 pairs of measurements. They inferred their dictum from the means of the cell-length and cell-angle distributions $N(\delta(y)_{ij})$ against $\delta(y)_{ij}$. I proceeded as follows, using a given many-site sample, with y_i and $u_{\rm exp}(y_i)$, of N measurements of a cell dimension. I compared many-site $u_{\rm sample}(y_i)$ with $\langle u_{\rm exp}(y_i) \rangle$; if the TK86 dictum holds, then this ratio should be about 5 for cell lengths and 3 for cell angles. However, if there are no systematic errors in the N measurements, then the many-site sample and single-site experimental s.u.s should be similar. Put another way, the measured values should fall within the band $\langle y_i \rangle \pm 3u_{\rm exp}(y_i)$ (see Fig. 5).

I conclude by comparing the s.u.s reported for the increasingly popular area detector methods with those obtained from 'routine' four-circle diffractometer measurements.

3. Current techniques for precise measurement of cell dimensions

The principles underlying the determination of high-quality values of the cell dimensions of single crystals were set out many years ago by M. J. Buerger (1937; this is a methodological paper, measured values not being reported) and then

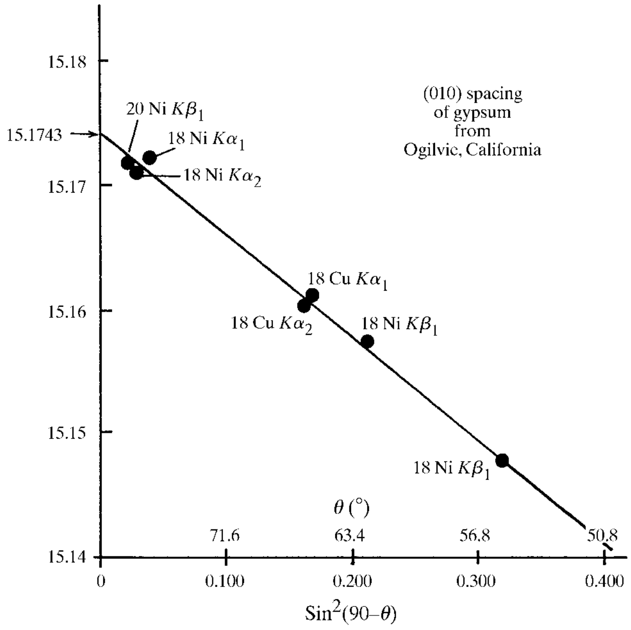

Figure 1
An example of Buerger's (1937, 1942) alloy-target, back-reflection Weissenberg, extrapolation to θ = 90°, technique. The precision is better than 1 part in 10^5; the highest-angle reflections have $\theta \simeq 82°$. The graphs also suggest that values of [010] calculated from spacings determined at $\theta \simeq 60°$(!) may well be in error by some 0.02 Å. The diagram has been slightly modified from Fig. 21 in Buerger (1942).

summarized in his classic monograph (Buerger, 1942). Contributions of that period by many others should surely also be remembered; I note only one classic paper, using polycrystalline samples, by Straumanis *et al.* (1960). As is well known, differentiating Bragg's equation gives $(\delta d/d) = -\cot\theta\, \delta\theta$, and thus spacing errors vanish as θ approaches 90°, even though errors in angle measurement remain finite. Thus, it is desirable that measurements be made over a range of angles as close as possible to 90°, and the derived dimensions then extrapolated to $\theta = 90°$; many different extrapolation functions have been used. An example from Buerger's laboratory is shown in Fig. 1. Other requirements are careful instrument alignment and specimen preparation and centring. These principles apply to both single-crystal and polycrystalline samples.

The most precise method for single crystals appears to be that of Bond (1960), which is based on the θ method of Weisz[5] *et al.* (1948) developed for oscillation photographs. Bond designed a special diffractometer for his work. Galdecka (1995, 1999) has drawn attention to the improvements made in the Bond method since its inception 40 years ago. The standard uncertainties quoted for the cell edges of sulfur (orthorhombic S_8), (D)-(+)-tartaric acid and some others (including corundum) are approximately 1–2 parts in 10^5, and for angles about 0.001° (Table 1). The back-reflection Weissenberg camera method, with measurements extrapolated to $\theta = 90°$, and sometimes using alloy X-ray tube targets (to give reflections at the highest possible angles), gave precisions of a few parts in 10^5 for cell lengths of inorganic crystals and of a few seconds of arc for cell angles (Buerger, 1937, 1942).[6] For a molecular crystal (hexabromobenzene), s.u.s of approximately 7 parts in 10^5 for cell edges and of $\sim 0.004°$ for angles were reported (Herbstein, 1963; Table 1). Standard four-circle diffractometers, used at high angles (thus foreclosing the use of Mo $K\alpha$ radiation unless the samples give reflections at high angles), but without extrapolation, have also been used. The Bond and back-reflection Weissenberg methods are capable of recording reflections close to $\theta = 90°$, while it is difficult to exceed $\theta \simeq 60°$ with standard diffractometers. Despite the 'high-θ' advantage of these two methods, it seems unlikely that techniques requiring tedious human intervention will be much used in these days of automated instrumentation.[7]

Considering random errors only, the standard uncertainty of a sample of N observations can be minimized by having the measurements as precise as possible [*i.e.* $\Sigma(y_i - \langle y_i\rangle)^2$ as small as possible], or by having N as large as possible, or by some combination of both; this is illustrated by (1), suitably adapted. The Bond method essentially depends on a small number of very precise measurements. The other methods depend to a varying extent on increasing N, and this is found in extreme form in some of the applications of area detector methods.

At this point I recount Kapteyn's illuminating and salutary 'Parable of the Chinese Emperor' taken from Parrish's (1960) report:[8] 'There...appears to be some confusion about the *reproducibility* of the results and the *accuracy* of the data...The exact height of the Emperor of China could be obtained by asking each of the 500 000 000 Chinese to guess his height. It was not necessary for any of his subjects to have seen him, or even his picture, because the application of statistical methods to so many individual observations would give an answer for the Emperor's height to a precision of a few microns or perhaps a few atomic diameters! It is clear that millions of measurements of say a table with a meter stick will not give an average measurement accurate to an Ångstrom unit' (the quotation has been slightly abridged).

Indeed, a simple calculation confirms Kapteyn's first estimate. Assume that the 5×10^8 guesses have a Gaussian distribution with mean 1.75 m and s.u. 0.083 m. The s.u. is obtained by assuming that the guesses span the range 1.50–2.00 m, with relatively few outliers; thus $6\,u \simeq 0.50$ m. The s.u. of the mean is thus $[0.083/(5 \times 10^8)^{1/2}]\, m \simeq 4\,\mu$, confirming Kapteyn's first estimate. A drastic increase in the population of China would be required for his second estimate to be correct.

The same point has been made by E. Bright Wilson (1952) in his classic 'An introduction to Scientific Research' (see §9.6 'Limits in Gain of Accuracy by Replication'). I ran together some trenchant remarks: 'Random errors can be reduced without limit by utilizing the mean of a larger and larger number of observations...this reduction [being] proportional to the square root of the number of observations...the practical limit on increasing accuracy by repeating observations...is set by the square root law.[9]...More serious, however, is the effect of systematic errors. These are not diminished by repetition and set a limit beyond which repetition is meaningless'.

There are a number of sources of systematic error, such as the variation of chemical composition among samples, variation of temperature, effects of absorption, and sample and instrumental misalignments. Systematic errors are assessed by comparing independent measurements (with regard to crystal sample, instrument, method, laboratory) of the same parameter, *i.e.* by using many-site methods.

An essential factor limiting precision is the nature of the specimen. Corundum (also as ruby) appears to be an example of a virtually ideal specimen – it is available in reproducible, chemically well defined form, hard, gives abundant reflections

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[5] Later Kennard.

[6] Although values of [010] (extrapolated to $\theta = 90°$) are given for gypsum and orthorhombic Sb_2O_3 (valentinite) in Buerger (1942), I have not been able to find Buerger's complete set of cell dimensions for either of these materials. Buerger's values are significantly different from those of Cole & Lancucki (1974; gypsum) and Svensson (1974; Sb_2O_3).

[7] Although a (double-radius) back-reflection camera is commercially available, I have not encountered reports of such measurements.

[8] Parrish acknowledges G. E. Uhlenbeck, who attributed the story to the Dutch astronomer J. C. Kapteyn (1851–1922). A referee has commented 'I am not sure the author is drawing the correct inference from the Parable...If the estimates of the citizens are all equally precise, and unbiased, observations from a common population, then the mean of that population is indeed known very precisely...but equating this mean to the actual height of the emperor...is a pure hypothesis, subject to further corroboration, or falsification'. An excellent point, but perhaps ascribing too much 'letter', and not enough 'spirit', to Kapteyn's parable.

[9] The computer revolution has reduced the importance of this aspect, so relevant in 1952.

at high diffraction angles (maximum $\sin\theta/\lambda \simeq 1.3$ Å^{-1}) and can be ground into small spheres. However, it appears to have limitations which have not always been taken into account (see below). Hopefully other metal and inorganic crystals of satisfactory diffraction quality will be found; a potential example is the zeolite used in the current IUCr round-robin study (Gabe, private communication, 1999). Oxalic acid dihydrate and anthracene are examples of good-quality organic specimens, obtainable in pure form (but oxalic acid dihydrate decomposes in air), which give reflections to medium (Mo $K\alpha$) diffraction angles ($\sin\theta/\lambda \simeq 0.7$ Å^{-1}). Clearly the precision attainable with these organics using standard methods (Mo $K\alpha$) can never match that attainable with corundum. Most organic and organometallic crystals have diffraction qualities lower than those of oxalic acid dihydrate and anthracene. Furthermore, the detailed nature of the diffraction pattern of a particular crystal may not permit equal precision in the determination of all six (in general) cell dimensions; hexabromobenzene (Table 1) is an example. Finally, I repeat that massive replication can never compensate for inherent limitations in specimen diffraction quality or measurement methodology.

4. Comparison of measurements of cell dimensions of corundum and ruby

4.1. Introduction

Among the most precise multiple measurements currently available are those for corundum; these were by Bond and four-circle diffractometer methods on single crystals, and by various techniques on polycrystalline samples. I discuss here many of the results reported to four significant figures after the decimal point (0.0001 Å), even though details of the experimental technique and standard uncertainties may be lacking. Some early results were summarized by Donnay & Ondik (1973).

I first considered the effects of temperature on the cell dimensions of corundum and then the effects of Cr^{3+} in solid solution (giving rubies of various compositions) in order to assess the importance of strict control of sample temperature and composition.

4.2. Thermal expansion of corundum and ruby

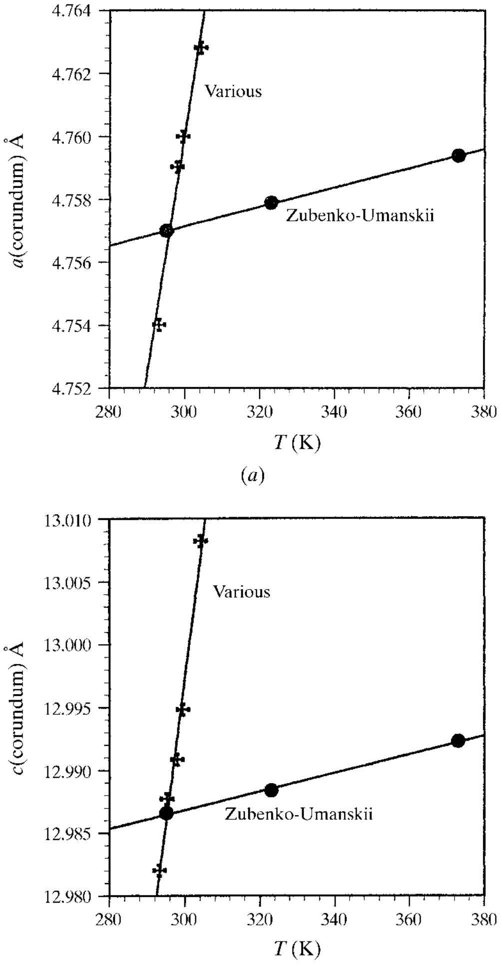
The cell dimensions and thermal expansion of corundum have been measured many times over the range 15–2000 K, but I am only concerned here with the region around room temperature. Measurements of a_T and c_T by Zubenko & Umanskii (1957; ZU57) on corundum are plotted in Fig. 2 for the restricted range 273–383 K;[10] there are similar results for ruby by Shal'nikova & Yakovlev (1956; SY56). Using a linear approximation, $a_{373} - a_{273}$ = (4.7596–4.7563) Å, *i.e.* Δa = 0.0036/100 = 0.000036 Å K^{-1}. Similarly, for the c axis, $c_{373} - c_{273}$ = (12.9923–12.9870) Å, *i.e.* Δc = 0.0053/100 = 0.000053 Å K^{-1}. Three other independent pairs of values for a and c covering the temperature range 293–304 K are also plotted in Fig. 2. In terms of these data, there are two possible temperature dependencies, differing roughly by factors of 20 and 50 (for the second, Δa = 0.0008 and Δc = 0.0024 Å K^{-1}). The larger temperature dependence (the linearity is presumably coincidental) is incompatible with the results obtained over the temperature range of ~1000 K and must be rejected. Thus,

$$a_{298}\,(\text{Å}) = a_T + 0.000036(298.15 - T) \qquad (3)$$

$$c_{298}\,(\text{Å}) = c_T + 0.000053(298.15 - T). \qquad (4)$$

4.3. Composition dependence of lattice parameters

Cell dimensions in the alumina–chromia series of solid solutions have been summarized by von Steinwehr (1967); there is a considerable spread of values. Not included in



(*a*)

(*b*)

Figure 2
Variation of (*a*) *a* and (*b*) *c* of corundum with temperature. The points labelled Zubenko–Umanskii have been extracted from a set of measurements by these authors (1957) covering the range 293–573 K. The points labeled 'various' are from Maslen *et al.* (1993; 293 K), Kirfel & Eichhorn (1990; 295 K), Cooper (1962; 298 K), Gabe (1981; 299 K), Shinoda & Amano (1950; 304 K).

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[10] As tabulated values were not given in many publications, I have had to read these values off enlargements of the published diagrams. The consequent loss of precision is unfortunate, but not vital when trends are being determined.

Steinwehr's survey were values from Linz & Newnham (1961; LN61), who measured (method not specified) cell dimensions over the whole composition range and found a linear dependence of both *a* and *c* on chromium content (given as mol % Cr_2O_3), *i.e.* there was obedience to Vegard's Law; Fig. 3. Similar (but less precise) results were reported by Spriggs & Bender (1962). A set of values showing a positive deviation from Vegard's Law has been given by Graham (1960; G60). Jan *et al.* (1960; JSD60) made measurements for the range 0–2%.

I have plotted the SY56, JSD60, LN61 and G60 values, and some others, in Fig. 4, showing only the 0–10% composition range. The first three of these sets agree well and the various 'single' values are also compatible. However, the G60 values are systematically larger than the other values, and the differences are well beyond possible errors in the XRD measurements. There are many hints in the literature of unusual behaviour in alumina–chromia solid solutions and the preparation of specimens is not necessarily straightforward. This is in accordance with the spread of values shown by von Steinwehr (1967) and in Fig. 4; a referee has commented that crystals grown by flame fusion suffer from annealing problems — often such crystals give excellent cell dimensions, but poor intensity measurements.

A linear fit over the complete composition range, based essentially on the LN61 values (Fig. 3), gives (C_m = mol % Cr_2O_3)

$$a\,(\text{Å}) = 4.7617 + 0.00208C_m; \quad R^2 = 0.995778 \tag{5}$$

$$c\,(\text{Å}) = 12.9830 + 0.00613C_m; \quad R^2 = 0.996889. \tag{6}$$

This is in good agreement with the equations given by JSD60 for the range 0–2%

$$\begin{aligned} a\,(\text{Å}) &= 4.7591\,(4) + 0.0024\,(1)C_m \\ c\,(\text{Å}) &= 12.9894\,(30) + 0.0059\,(4)C_m. \end{aligned} \tag{7}$$

Thus, 1 mol % Cr_2O_3 is approximately 58 times as effective in changing the *a* dimension as a 1 K rise in temperature; the

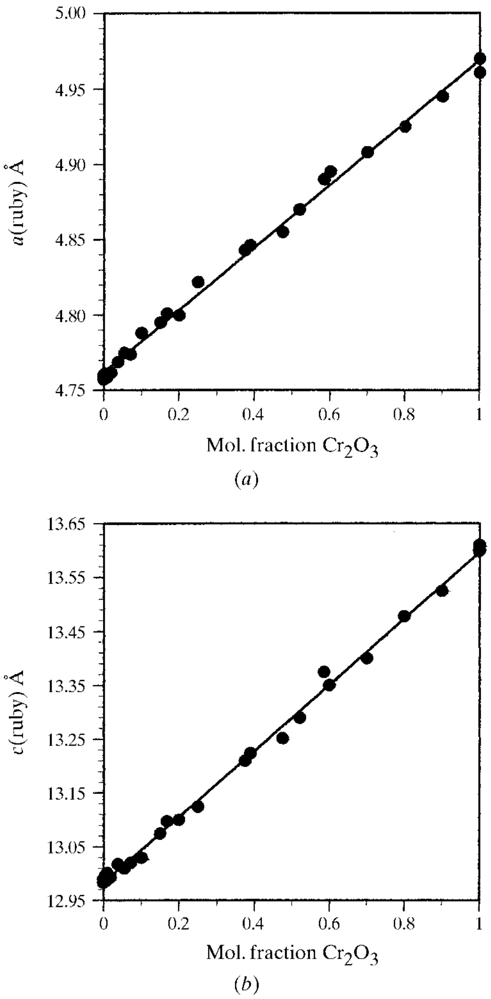

Figure 3
Cell dimensions (*a*) *a* and (*b*) *c* of rubies as functions of chromia content across the whole range of solid solutions. Most of the points have been read from Fig. 1 of Linz & Newnham (1961), but points from other authors (see Fig. 4) have been included in the 0–0.12 mol. fraction range.

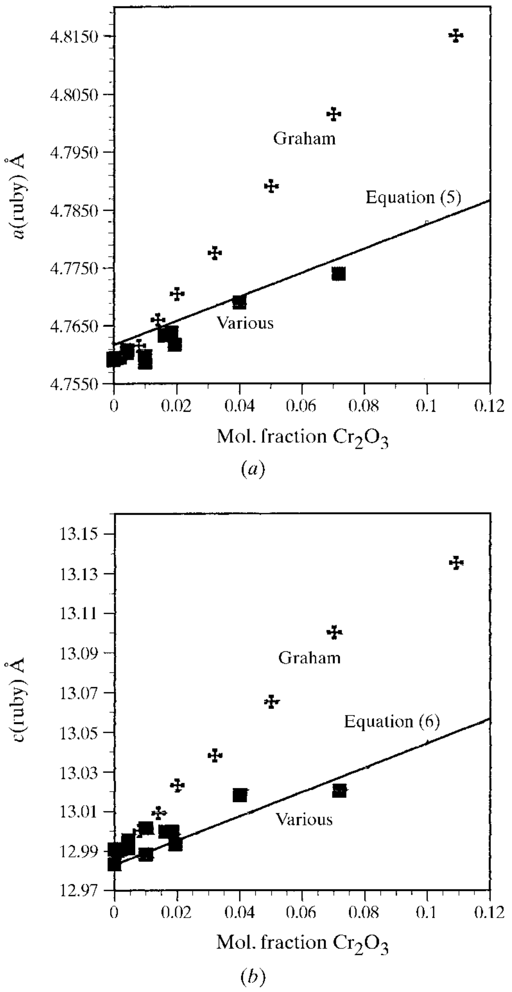

Figure 4
The 0–0.12 mol. fraction Cr_2O_3 range of Fig. 3, (*a*) *a* and (*b*) *c*, has been expanded in order to show that most measurements are compatible with equations (5) and (6) (and the equations of JSD60), but that the measurements of Graham (1960) are discrepant. 'Various' includes single values given by Estifanos *et al.* (1997) and McCauley & Gibbs (1972); the full list is given in Table C (deposited).

corresponding figure for c is 116. It follows that it is most important to control composition and that the effect of temperature is secondary.

4.4. Results for corundum

The most precise results were obtained using the Bond method (Cooper, 1962). The c axis was derived from $d(00.12)$, measured with Fe $K\alpha_1$ (λ = 1.932076 kX). Then $d(40.8)$ was measured with Cu $K\alpha_1$ (λ = 1.537395 kX) and a was calculated by combining c and $d(40.8)$; for both reflections, $\theta \simeq 63°$. Four measurements of θ were made for each reflection, single-site $u_{\rm sample}(\theta)$ was 0.0006 and 0.0021° for the two reflections, and refraction corrections (see below) were made for both reflections. The Cooper corundum sample had 0.008% Cr and trace amounts of other transition elements. The results [at T = 297.85 (10) K] were a = 4.759296 (27), c = 12.991576 (242) Å, where $u_{\rm exp}(y_i)$ is bracketed [the conversion factor kXu to Å is 1.00207683 (29), see Table 4.2.2.6 of *International Tables for Crystallography*, 1999, Vol. C, 2nd ed.].[11] The values appropriate to pure corundum at 298.15 K are a = 4.759288 (27) and c = 12.991544 (242) Å. The precision is 0.6 parts in 10^5 for a and 1.9 in 10^5 for c, or approximately 1 part in 10^5. These values serve as the standards for comparison with other measurements.

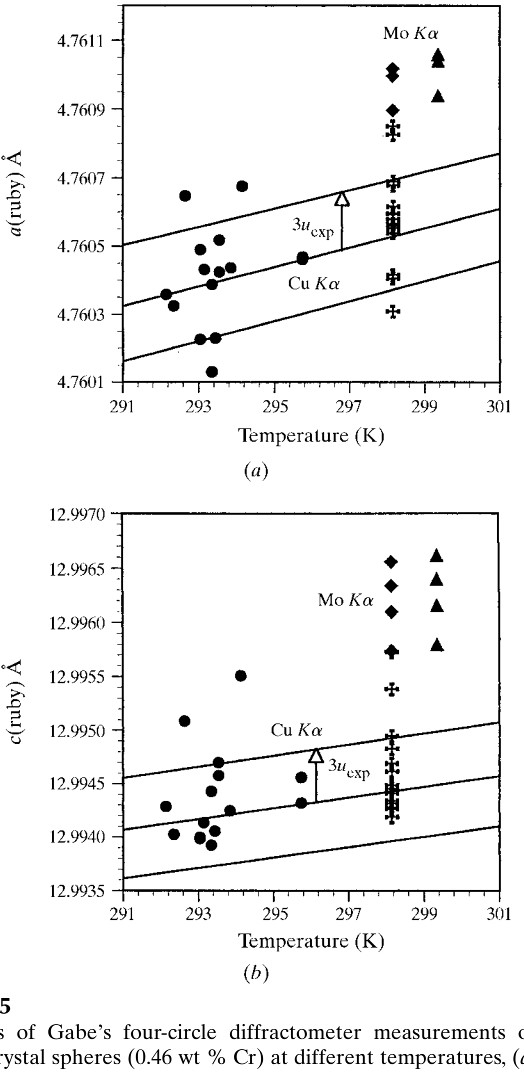

Figure 5
Analysis of Gabe's four-circle diffractometer measurements on ruby single-crystal spheres (0.46 wt % Cr) at different temperatures, (a) a and (b) c. The filled circles show the actual results as measured with Cu $K\alpha_1$ and the line of crosses represent these values corrected to 298.15 K, according to the linear thermal expansion approximations shown in Fig. 2. Analogous values for Mo $K\alpha_1$ are shown on the right-hand sides of the diagrams. The $[\langle y_i \rangle \pm 3\langle u_{\rm exp}(y_i)\rangle]$ bands are shown; most results fall within these limits, but there are a few outliers. It is not clear why the Mo $K\alpha_1$ results are significantly larger than those by Cu $K\alpha_1$.

A CAD-4 four-circle diffractometer was used by Gabe (1981; Table A1 of deposited[12] material) for measurements (Mo $K\alpha_1$, λ = 0.70932 Å; T = 299.35 K) on corundum crystal spheres (described as 'pure Al_2O_3'), but full details have not been given.[13] The results (I have corrected the values quoted by Thompson *et al.*, 1987, to 298.15 K) were a = 4.758956 (3) and c = 12.994746 (70) Å. There are highly significant differences between the Cooper and Gabe values for a and c (Δ/u = 0.000332/0.000027 = +12.9 for a and −0.003206/0.000242 = −12.5 for c; Δ = Cooper − Gabe). As the differences are in opposite directions, they cannot be ascribed to the lack of refraction corrections for the Gabe measurements.

4.5. Results for ruby

A CAD-4 four-circle diffractometer was used by Gabe (1981; Tables A1 and A2, deposited) for measurements on ruby crystal spheres [Al_2O_3 containing 0.46 (3) wt % Cr]. With Cu $K\alpha_1$ (λ = 1.54060 Å) there were 15 sets of measurements (98–101 reflections with θ between 61 and 68°) on 12 crystals, three sets being duplicates on three different crystals; the measurement temperatures varied from 292.15 to 295.75 K; $\langle u_{\rm exp}(a)\rangle$ = 0.000060 and $\langle {\rm u}_{\rm exp}(c)\rangle$ = 0.000166 Å.[14] The a and c values for the crystals used have been plotted against temperature in Fig. 5; most values lie within the $\langle y_i \rangle \pm 3 \langle u_{\rm exp}(y)\rangle$ band, which has been given the appropriate (thermal expansion) slope from (1) and (2). Individual values have been corrected for thermal expansion and plotted at T = 298.15 K in Fig. 5; the mean values are a = 4.760585 (144) and c = 12.994637 (436) Å at 298.15 K. The values of (many-site) $u_{\rm sample}(y_i)$ (in brackets) are 2.4 and 3.8 times as large as (single-site) $\langle u_{\rm exp}(y)\rangle$.

Similar measurements were made (by Gabe) for four different ruby crystals at 299.35 (10) K using Mo $K\alpha_1$ (λ = 0.70932 Å; for each crystal 74 reflections with θ between 52.5 and 60° were used); $\langle u_{\rm exp}(a)\rangle$ = 0.00005 Å and $\langle u_{\rm exp}(c)\rangle$ = 0.00016 Å. After the temperature corrections as detailed above, I obtained (both sets at 298.15 K) for the Mo $K\alpha_1$

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[11] As has been often noted in the past, it is incumbent on an experimenter striving for the highest precision in measurements of cell dimensions to state explicitly the values used for X-ray wavelengths.

[12] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK0071). Services for accessing these data are described at the back of the journal.

[13] The provenance of Gabe's results is as follows: at the 1981 IUCr Congress and General Assembly in Ottawa, participants were given small single-crystal ruby spheres [Al_2O_3 containing 0.46 (3) wt % Cr], together with the results of four-circle diffractometer measurements made on four different spheres (Gabe's detailed description of the experimental results is deposited here as Tables A1 and A2, with his permission).

[14] For the three duplicates we find $\langle \Delta(a,c)/(u_1^2 + u_2^2)^{1/2}\rangle$ = 0.80. This indicates that $u_{\rm exp}(y)$ has been correctly assessed.

measurements: a = 4.760952 (64) and c = 12.996181 (351) Å. These two sets of values are also entered into Fig. 5. The values of (many-site) $u_{\rm sample}(y_i)$ (in brackets) are 1.2 and 2.2 times as large as (single-site) $\langle u_{\rm exp}(y)\rangle$.

The Mo K values are both slightly larger than the Cu K values; I tested whether the differences are significant using the Fisher–Behrens statistic described by Hamilton (1964). The null hypothesis gives $\langle y_{\rm Cu}\rangle = \langle y_{\rm Mo}\rangle$. For a and c I find that u = 7.0 on 21 degrees of freedom, and 2.9 on 14 degrees of freedom, respectively. Using Student's t test both values lead to a highly significant rejection of the null hypothesis. I do not know why different radiations should give significantly different results. Approximate corrections for refraction (based on Cooper, 1962; a = 0.000081 and c = 0.000222 Å for Cu $K\alpha$ and 0.21 for Mo $K\alpha$) are not large enough to eliminate the differences. It would be of interest to apply the appropriate statistical tests to the measurements of Siegrist *et al.* (1999) to check whether there are systematic differences among groups characterized by diffractometer, wavelength, crystal *etc.*

For 0.46 wt % Cr (which is 0.50 mol % Cr_2O_3), one would expect an increase in a of 0.0010 Å and of 0.0031 Å in c; the measured values (averaging over Cu and Mo) are 0.0017 and 0.0046 Å, 1.7 and 1.5 times as large as the expected values, respectively.

4.6. Other measurements on corundum and ruby

Measurements have been reported (Siegrist *et al.*, 1999) on a series of 42 rubies on four different four-circle diffractometers. After correction for thermal expansion and refraction, the mean was a = 4.76080 (29) and c = 12.99568 (87) Å; the bracketed values are 'expanded uncertainties', which are s.u.s multiplied by an unstated coverage factor, presumably 2 or 3 (Taylor & Kuyatt, 1994). Parallel Guinier camera measurements on ruby powders (Cox *et al.*, 1981) gave a = 4.76093 (31); c = 12.9959 (23) Å. The results have s.u.s of some parts in 10^5.

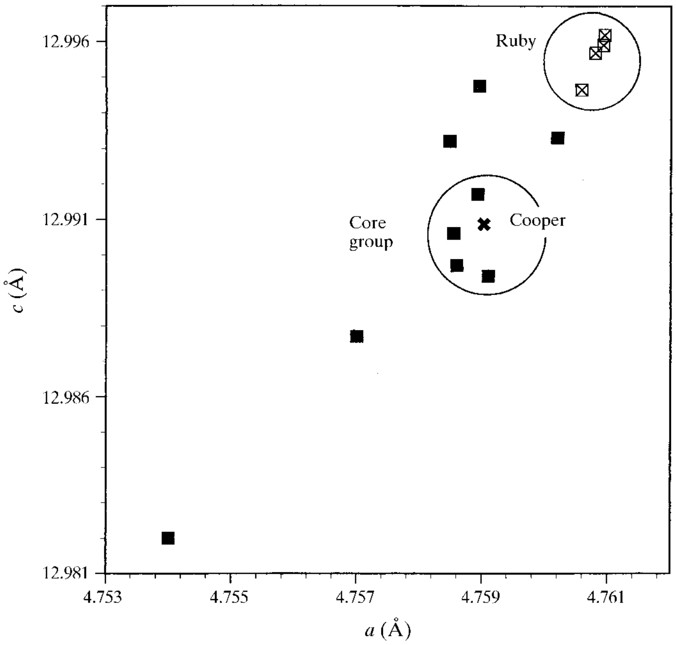

Figure 6
Plot of c (Å) against a (Å) for the corundum (filled squares) and ruby (crossed squares) samples detailed in Table B (deposited). The Cooper standard values are marked by a cross; the s.u.s of the measurements are all smaller than the data points. The corundum core values and the ruby values are enclosed in circles.

My colleague Dr M. Kapon has used one of the 'Ottawa' ruby spheres for alignment of a Philips PW1100/20 four-circle diffractometer in our laboratory, the conditions being chosen to resemble those used for routine measurements on molecular crystals. The following mean results were obtained from eight sets of measurements (Mo $K\alpha$, 25 reflections with $\theta_{\rm max} \simeq 20°$; $T_{\rm nominal}$ = 295 K) carried out over a period of 15 months (the rhombohedral crystal was treated as triclinic): a = 4.766 (3), b = 4.765 (3), c = 13.013 (7) Å, α = 90.00 (4), β = 89.99 (4), γ = 120.03 (5)°; the sample s.u.s are bracketed and are about 60 parts in 10^5 (experimental s.u.s are not given by the programme available to us). These results agree with those of Gabe within the errors quoted, but the sample s.u.s are approximately 50 times as large as those given by Gabe.

4.7. Conclusions from the analysis of the results for corundum and ruby

The precision of the Cooper measurements (Bond diffractometer) for corundum is approximately 1 part in 10^5. The precision of the Gabe and Siegrist four-circle diffractometer measurements on ruby is about 3–7 parts in 10^5. The similarity is perhaps deceptive because Cooper used eight very precise angle measurements to determine two parameters, while Gabe's diffractometer measurements[15] on ruby are characterized by large values of N; with Cu $K\alpha_1$ 100 reflections were measured on 12 crystals (with an additional three duplicates), *i.e.* 1500 measurements to determine two parameters, while with Mo $K\alpha_1$ 74 reflections were measured on four crystals, *i.e.* 300 measurements to determine two parameters. One cannot escape the 'Parable of the Chinese Emperor.'

Powder and single-crystal measurements on corundum and ruby have been collected together in Fig. 6 (see also deposited Table B), the claimed precisions ranging between a few parts in 10^5 and a few parts in 10^4. The values can be divided into two groups – a core group where the a and c values cluster round the Cooper 'standards', and a group of outliers. It seems that new measurements by diffractometer (four-circle or powder) or high-class camera techniques will yield values close to those of the core group and that there is little to be gained from additional effort in this direction unless particular attention is paid to specimen preparation. The Law of Diminishing Returns, if not already in operation, appears to be close at hand. Rather similar conclusions apply to ruby. Independent Bond diffractometer measurements on rubies of different compositions (with requisite care in specimen preparation) may have something to contribute. A referee has commented (in connection with the sample quality problems

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[15] Details of the Siegrist measurements are not yet available.

Table 2

Unweighted mean values for cell dimensions (Å, °) of α-oxalic acid dihydrate at room temperature (four independent sets of measurements) and 100 K (seven independent measurements), and for anthracene at room temperature (five independent sets) and 95 K (five independent sets).

The sample (many-site) s.u.s are in square brackets and mean experimental (single site) s.u.s in round brackets.

T (K)	a	b	c	β
α-Oxalic acid dihydrate				
295†	6.1183 [22] (23)	3.6045 [26] (15)	12.0538 [38] (30)	106.298 [22] (20)
100†	6.1021 [44] (22)	3.4998 [51] (11)	11.9603 [133] (28)	105.772 [62] (20)
Anthracene				
295†	8.5592 [53] (58)	6.0268 [106] (62)	11.1730 [75] (63)	124.653 [52] (59)
95†	8.4195 [143] (41)	5.9951 [92] (47)	11.1042 [137] (49)	125.322 [185] (51)

† Nominal temperature.

mentioned above) that it is to be hoped that the (current IUCr) ruby survey 'will include studies of the cell parameters of different ruby spheres performed on the same instrument, the same ruby performed in different laboratories as well as different rubies examined on different instruments'.

The ranges given in the previous paragraph are considerably wider than the values quoted above for the standard uncertainty of the experimental diffractometer measurements [§4.5; $u_{\rm exp}(y_i)$] and thus the TK86 dictum applies to the suite of values for corundum (and presumably also to ruby, although here less information is available).

5. Comparison of single-site and many-site four-circle diffractometer cell dimension measurements for molecular crystals

5.1. α-Oxalic acid dihydrate

A comprehensive set of results over a range of temperatures has been extracted from the CSD and deposited (Table D). These values are shown in Fig. 7; it is obvious that the multiple room-temperature results cluster more closely than those obtained at ~100 K. I have calculated means and (many-site) sample s.u.s for the 295 and 100 K results (Table 2). The sample s.u.s are about 50 parts in 10^5 at room temperature and 2–3 times as large at 100 K; the corresponding values for angles are 0.02 and 0.06°.

5.2. Anthracene

A similar procedure has been followed for anthracene [Table E (deposited) and Table 2]. The sample s.u.s for cell edges are approximately 80 parts in 10^5 at room temperature and 2–3 times as large at 95 K; the corresponding values for angles are 0.05 and 0.19°. In their Fig. 1, Brock & Dunitz (1990) show the much larger spread of values at 95 K compared with 298 K.

5.3. Conclusions

I conclude that, at room temperature, measures of single-site (experimental) and many-site precision agree reasonably well for both α-oxalic acid dihydrate and anthracene and thus the TK86 dictum appears to be too conservative. However, this is not so at 100 K, where there is a discrepancy of a factor of ~5 (for cell edges) and 3 (for angles) between single-site and many-site s.u.s. As (mainly) the same groups of investigators carried out both room-temperature and 100 K sets of measurements (on one or other of the crystals), the discrepancies should probably be ascribed to various of the experimental difficulties involved in low-temperature measurements. I quote from one of the referees 'essentially what seems to be happening...is that at room temperature, with a properly aligned diffractometer, a properly centred crystal, and with diffractometer concentricity all in decent form, the s.u. values are [good] estimates of the accuracy of the cell constants. At lower temperatures, systematic errors (uncentred crystal, crystal moving with the

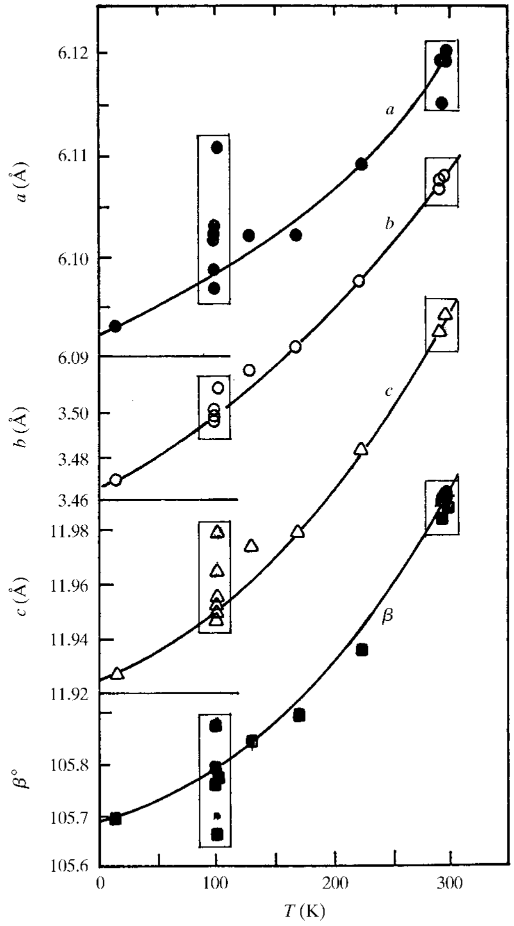

Figure 7

Cell dimensions of oxalic acid dihydrate from many sources (see Table D for details) plotted as a function of T (K). The values at ~295 K (4 sets) and ~100 K (7 sets) are boxed for emphasis; note the greater spread of the latter compared to the former. The curves have no physical significance and are only guides to the eye.

Table 3
Two examples of cell dimensions (Å, °) determined by area detector methods (Mo $K\alpha$ radiation).

Method	a/α	b/β	c/γ	No of reflections used and θ range (°)	Reference
SMART	8.8144 (1)	9.1481 (1); 97.827 (1)	27.8748 (2)	8192; 2.0–18.0	†
Stoe IP	7.567 (11); 72.00 (8)	9.297 (13); 80.21 (8)	12.281 (14); 81.04 (8)	397; 9.5–56.3	‡

† Muneer *et al.* (1997): the values given are for their compound (2a), but very similar values are given for compound (2b). ‡ de Castro *et al.* (1997).

flow of gas and uncertain crystal temperature) creep in and the s.u. values are no longer reliable'.

The highest *claimed* precision that I have encountered for (apparently routine) four-circle diffractometer measurements is 1–2 parts in 10^5 for cell edges, and 0.005° (CAD-4 diffractometer, 295 K, Mo $K\alpha$, θ range 10.86–17.89°; Tahir *et al.*, 1997). As no special measurement techniques are described, it is difficult to believe that these s.u.s have any physical significance.

6. Cell dimensions by area detector methods

In contrast to the four-circle diffractometer method, where there is a very considerable standardization of both methodology and results [for example: Mo $K\alpha$, 25 reflections, u(length) $\simeq$ 10–100 parts in 10^5, u(angle) $\simeq$ 10–30 $\times 10^{-3\circ}$], there is a variety of approaches to the determination of cell dimensions by area detector methods. I have summarized in Table G (deposited) information obtained from issues 10 and 11 of *Acta Crystallographica* C**53** (1997); there are 15 entries. Table 3 gives two contrasting examples which have been chosen to illustrate the largest and smallest s.u.s in the group of Table G. In this sample the number of reflections used ranges from 27 to 96 914 and the precisions claimed range from 130 to 1 parts in 10^5 for cell lengths and from 0.080 to 0.001° in angles. I have also scanned *Organometallics*, Volume 18, No. 17 (August 16, 1999). Cell dimensions are generally given with edge-length s.u.s of a few parts in 10^5 and angle s.u.s around some thousandths of a degree, suggesting uncritical reproduction of computer printouts. The procedures used for calculating s.u.s are not in the public domain as they are components of proprietary software, but it seems inconceivable that precisions can approach those of the Bond method. A more realistic estimate surely comes from a recent analysis of a 'modern imaging diffractometer' (Paciorek *et al.*, 1999), where u(length) is given as 10 parts in 10^5 and u(angle) as $10 \times 10^{-3\circ}$.

7. Discussion

Good diffractometer and crystal alignment, especially precise positioning of the θ-angle zero, and good centering of the crystal (Dera & Katrusiak, 1999) are crucial requirements for good quality measurements. Some modern cell dimension refinement programs include crystal position as a variable; whether this is to be considered as progress is debatable. Reflected beam displacements (and hence errors in θ) owing to alignment deficiencies (and crystal absorption) are more important at low θ angles and this is the argument for basing determination of cell dimensions on reflections at larger θ angles (which for most organic and organometallic crystals are unlikely to much exceed 30° at 295 K, using Mo $K\alpha$). The $\alpha_1 - \alpha_2$ splitting (Mo $K\alpha$) in θ is 0.2° at θ = 30° ($\Delta\lambda/\lambda \simeq$ 600 parts in 10^5) and thus the definition of the effective wavelength used becomes important above 30°. Most diffractometer measurements of cell dimensions are made before intensity measurements begin and generally little is known at that stage about the existence (or absence) of reasonably strong reflections at higher angles. However, these could be found by a rapid scan through the reciprocal lattice and this is standard practice in some laboratories. Alternatively, or in addition, a second set of measurements could be made after collection of intensities has been completed; crystal stability is required. Most sets of measurements are analyzed assuming a particular symmetry for the crystal. There is much to be said for a two-stage approach – first carry out the analysis as if for a triclinic crystal and then impose the appropriate symmetry. This would provide an internal assessment of the precision of length and (especially) angle determinations. There is one remedy to the problems stemming from the widespread use of Mo $K\alpha$ for solving crystal structures – using Cu $K\alpha$, with its advantages of reflections at higher angles, to determine cell dimensions and then measure intensities with Mo $K\alpha$. Easy realignment of a diffractometer after tube replacement is a *sine qua non*.

It seems that the TK86 dictum is somewhat severe for high-purity, good diffraction-quality crystals measured at room temperature by standard four-circle diffractometer methods. However, the dictum seems appropriate to low-temperature measurements even when the constraints noted do apply. It would also seem safe, conservative practice to apply the dictum whenever measurement conditions are not optimal. Standardization of area-detector methods of measuring cell dimensions seems to be a matter requiring urgent attention; published s.u.s from such methods should be viewed with considerable (perhaps 'utmost') suspicion.

To sum up, there is a hierarchy of precisions in single-crystal (and powder) cell dimension measurements. The highest precisions (some parts in 10^5) originate from Bond diffractometer measurements; Buerger back-reflection Weissenberg measurements show similar precision after extrapolation to θ = 90°, followed by *careful* four-circle diffractometer and powder measurements. 'Routine' four-circle diffractometer measurements will give precisions of some parts in 10^4 under optimal conditions. Analysis suggests that similar precisions should be obtainable with imaging diffractometers, but little (or no) reliance can be placed on currently reported s.u.s from such diffractometers.

Table 4
Comparison of some early cell dimension values with those measured by Cooper (1962) using the Bond diffractometer (values in kX).

References are given by Cooper (1962).

Crystal	Cooper (1962)	Early result	Reference
Al	a = 4.04143 (2)	4.04139 (8)	Jette & Foote (1935)
Ge	a = 5.64613 (1)	5.64607 (4)	Straumanis & Aka (1952)
Quartz	a = 4.90333 (1)	4.9029	Bradley & Jay (1933)
	c = 5.39395 (3)	5.3933	

Perhaps the most remarkable feature of cell dimension measurements is how little the claimed precisions have changed over a period of 40–60 years. This is shown in Table 4, where some early results (taken from Cooper, 1962) are compared with her Bond diffractometer measurements.

Note added in proof: Guy *et al.* (1982) used a back-reflection Weissenberg method to determine d^{100}, d^{010} and d^{001} for two triclinic crystals over the temperature range 300 to 10 K [Cu $K\alpha$, θ (Bragg) > 80°; estimated precision 3 parts in 10^4].

I am grateful to Dr E. J. Gabe (Ottawa) and Dr M. Kapon (Haifa) for permission to use unpublished results, and to Dr Gabe for helpful discussions. I have also incorporated many of the helpful comments of three anonymous referees.

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