On the significance of small deviations from higher symmetry

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ABSTRACT

Small deviations from higher symmetry can be established by single-crystal diffraction methods by (1) measuring the metric of the unit cell with high, non-routine precision; (2) measuring a full reflection sphere of diffraction data and testing it for the presence or absence of symmetry elements in the dataset; (3) refining the structure in both the higher and the lower symmetry and comparing the results; (4) checking the refined crystal structures for the presence or absence of hidden symmetry elements. By these criteria it is not established that the v{120} growth sector of yugawaralite really has triclinic symmetry (Tanaka *et al.*, 2002). On the contrary, the refined metrical parameters and the atomic positions conform to monoclinic symmetry within the margins of experimental error.

Introduction

NUMEROUS crystal structures have been refined by single-crystal diffraction methods in unnecessarily low symmetry and then subsequently published. Lists of falsely determined structures are available in the literature; see e.g. Baur and Kassner (1992) and Marsh *et al.* (2002), where additional references on this topic can be found. It has been estimated that ~3% of all determined crystal structures were described with symmetry that is too low (Baur and Tillmanns, 1986). This problem has even found attention in advanced textbooks (Stout and Jensen, 1989). The vast majority of the cases discussed in the references given above concern unintended experimental mistakes. However, most of the lessons learned in analysing these errors can be applied in instances where one wishes to test the symmetry of a particular sample, because one has reason to think that its symmetry is actually lower than previously assumed. The advantage one has in such cases is that the X-ray diffraction (XRD) experiment can be planned ahead of time in such

a way that the hypothesis of presumed lower symmetry can be tested as fairly and as unequivocally as the experimental ambiguities will allow. Since we realize that the strategies to be followed when pursuing this course are not all that well known, we give first a short overview of the subject and then apply the principles to the low-symmetry refinement recently published in this journal (Tanaka *et al.*, 2002).

Changes of crystal system and Laue class

While there are three main ways of lowering the symmetry of a crystal structure, we shall concentrate here on category 1 of Baur and Tillmanns (1986), which is the case where the crystal system and consequently the Laue class as well are changed.

(I) Deviations of the metric of a lattice

In order to show by experiment that a particular sample has a lower symmetry than previously assumed we have to be certain of the metric of the lattice by measuring it with high precision. That means that a routine unit-cell determination on a single-crystal diffractometer alone is insufficient. It has been shown that in routine cell-parameter

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determinations, the estimated standard deviations (e.s.d.s) are grossly underestimated by a factor of 5 for cell lengths and by a factor of 2.5 for cell angles (Taylor and Kennard, 1986; Herbstein, 2000). If the observed deviations from higher symmetry are small, great care must be taken in determining the cell dimensions by using either precise powder diffraction methods or for single crystals the back-reflection Weissenberg camera or the Bond method (Bond, 1960). Even on a standard single-crystal diffractometer one can improve the precision by being extremely careful about orientation and centering of the crystal (an inaccurate centering of the specimen on a diffractometer might simulate an apparently lower symmetry) and by using only reflections at the very highest diffraction angles. If and when the cell dimensions of a sample deviate significantly, i.e. clearly beyond experimental errors, from the restrictions imposed by a previously assumed crystal system of higher symmetry, the hypothesis of lower symmetry is proved.

(2) Symmetry of the set of diffraction data

Even if there is no deviation in the lattice symmetry of the crystal, its overall symmetry could still be lower than originally assumed. Such instances are rare, but they do occur (e.g. when a monoclinic angle has a value very close to 90°, e.g. a monoclinic aluminogermanate with β = 90.000(2)°, Tripathi *et al.*, 2000). In such cases, especially when the question involves a possible triclinic symmetry, a complete reflection sphere has to be measured. The diffraction data have to be merged according to the various assumed symmetries, and the presence or absence of symmetry in the set of diffracted data has to be tested by comparing the resultant internal agreement factors (R_{merge}). In view of the usually low precision of individual structure factor measurements, the results might be ambiguous, particularly when the deviation from the higher symmetry is small.

(3) Refinements in several possibly applicable space groups

The variously merged data sets have to be refined in both the space groups of higher symmetry and those of lower symmetry and the results compared with each other. A check on the agreement factors (*R* values) and the statistical errors (e.s.d.s) is useful at this stage. Examples for this procedure

are available in the literature (Baur and Ohta, 1981; Baur *et al.*, 1997).

(4) Checking the symmetries of the refined crystal structures

After the crystal structures have been refined, they can be checked for the presence or absence of higher symmetries, either by a direct inspection of atomic positions and bond lengths and angles or by applying a computer program such as MISSYM (Le Page, 1988). In this way it can be ascertained that the lower symmetry structure really has a lower symmetry and does not contain hidden symmetry elements not assumed by the space group of lower symmetry. This is the usual method of diagnosing crystal structures accidentally determined in unnecessary low symmetry as discussed above in the introduction.

Symmetry of growth sectors of yugawaralite

On the basis of optical observations of the growth sector v{120} it was concluded by Tanaka *et al.* (2002) that this sector is optically triclinic, while the growth sector k{011} was found to be optically monoclinic. Single-crystal X-ray structure determinations of both specimens were interpreted as showing that indeed the crystal structures of these two parts of a yugawaralite crystal were triclinic (space group *P*1) and monoclinic (space group *Pc*), respectively.

The following discussion of the evidence for the triclinicity of the v{120} sample is keyed to the points 1–4 above.

(1) The unit-cell parameters of the two samples were measured in Tanaka *et al.* (2002) by routine methods employing 25 reflections in the range of 20<2θ<27° for k{011} and 24 reflections in the range 20 < 2θ < 30° for v{120}. The measured values for the parameters are (k{011} always first, v{120} second): *a*, 6.711(1) Å and 6.710(1) Å; *b*, 13.969(1) Å and 13.985(2) Å; *c*, 10.027(1) Å and 10.032(2) Å; α, 90° and 89.96(1)°; β, 111.16(1)° and 111.14(1)°; γ, 90° and 90.01(1)°. When and if the differences between the individual parameters and their e.s.d.s are taken at face value, the cell constants *b* and the angles α are significantly different for the two specimens. However, keeping in mind Taylor and Kennard's (1986) dictum that the e.s.d.s of the cell lengths have to be multiplied by a factor of 5 and those of the angles by 2.5, these differences become insignificant, since the values for k{011} and v{120}are

within ~1.5 e.s.d.s of each other. For all practical purposes the metric of the v{120} lattice is monoclinic, as it is for the k{011} lattice. In general the angles α and γ, experimentally determined from a subset of reflections, deviate from 90° even in the monoclinic case. They must be set by hand to match the metrical constraints of the crystal system. Since the experimental values for the k{011} structure are not given, the conclusions drawn by the authors cannot be verified.

(2) The paper by Tanaka *et al.* (2002) reports no evidence of an analysis of the symmetry of the set of diffraction data. Whether a whole reflection sphere was measured or not is not stated. Thus, the diagnosis has to proceed without this information. It is interesting to note, however, that the structure factors calculated from the atomic data (using SHELXL-93, Sheldrick, 1993) published by Tanaka *et al*. (2002) clearly indicate the presence of a *c* glide plane. All F_c^2-values of *h0l* reflections with l being odd are <0.0096% of the strongest reflection and consequently should be considered as systematically absent.

(3) A refinement of the v{120} specimen in space group *Pc* is not reported in Tanaka *et al.* (2002). The *R* value given for the triclinic refinement of v{120} is clearly higher than for the monoclinic refinement of k{011}, but this difference is not discussed. Thus, the diagnosis has to be made without benefit of this kind of information.

(4) As evidence of the triclinicity of the v{120} sample, Tanaka *et al.* (2002) give in their Table 6 the values of 11 pairs of bond distances and angles which would be identical by symmetry in space group *Pc*, but are different in *P*1, e.g. Al(1a)–O(7b) 1.755(6) Å and Al(1b)–O(7a) 1.729(6) Å (this is the largest percentage deviation for any of these pairs). We calculated the same values using the unit-cell constants from Table 2*b* and the atomic coordinates from Table 4*b* of Tanaka *et al.* (2002) and obtained Al(1a)–O(7b) 1.76(3) Å and Al(1b)–O(7a) 1.73(3) Å. Inasmuch as all e.s.d.s of the *x*, *y* and *z* coordinates of the Si, Al and O atoms in Table 4*b* have a value of 0.002, all the e.s.d.s of the atomic positions amount therefore to ~0.02 Å and the e.s.d.s calculated by us for the bond lengths are of the correct magnitude. Thus, keeping in mind their possible statistical errors, the comparison of these 11 pairs does not support a triclinic symmetry for v{120}. We made a complete comparison of all atomic positions of the triclinic structure by using the 58 triples of atomic coordinates reported by Tanaka *et al.* (2002) in the refinement in space group *P*1 for a distance calculation in space group *Pc*. In this way we saw the distances of all the atoms to their 'triclinic' counterparts. These distances range from 0.03 to 0.09 Å with a mean value of 0.063 Å and an e.s.d. of the individual value of 0.04 Å. This becomes even clearer by calculating the distances Δ*d* (column 7 in Table 1) between the monoclinic positions (averaged from the respective triclinic positions) and the corresponding triclinic counterparts expressing the effective deviation of the triclinic structure from monoclinic symmetry for the individual atoms. Accordingly, the mean deviation from monoclinic symmetry is 0.031 Å. It is interesting to note that the longest principal axes of the thermal ellipsoids (column 8 in Table 1) are, on average, more than five times longer than the spatial separation between the atoms in the monoclinic and the triclinic settings. This shows unambiguously that within the statistical error of the crystal structure analysis performed by Tanaka *et al.* (2002), the v{120} structure is monoclinic and not triclinic because the distances between the triclinic pairs are, on average, only within 1.6 e.s.d.s from each other and the distances of the atoms in the monoclinic structure are within 1.14 e.s.d.s of their corresponding triclinic positions.

Symmetry of growth sectors of edingtonite

For edingtonite, Tanaka *et al.* (2002) measured the unit-cell constants and suggest that the growth sector *m*{110} of edingtonite is triclinic, while the growth sector *c*{001} is orthorhombic. Using the same reasoning as above it seems that neither case has been made. The *a* and *b* cell lengths of the two sectors deviate by <1 e.s.d. from their mean value, indicating that their deviation from tetragonal is insignificant. The deviations of the unit-cell angles from 90° are, on average, smaller than 1.5 e.s.d.s (in both cases we are assuming Taylor and Kennard's, 1986 dictum).

Optical anomalies

Symmetry deviations of optical properties from the ideal symmetry of crystals are called optical anomalies. Such anomalies were observed by Tanaka *et al.* (2002) on yugawaralite and were the starting point for their crystal structure determination. The effect is well known and described, e.g.

TABLE 1. Atomic parameters for the growth sector v{120} of yugawaralite in space group Pc obtained from the averaging of the coordinates and the displacement factors given for space group $P1$ by Tanaka *et al.* (2002); a, 6.710(1) Å; b, 13.985(2) Å; c, 10.032(2) Å; α, 90°; β, 111.14(1)°; γ, 90°, all atoms are in Wyckoff position 2(a) with site symmetry 1. Coordinates are given corresponding to the setting after Tanaka *et al.* (2002) with standard names as defined by Baur and Fischer (2000). Δd is the distance (with e.s.d.s in parentheses) between the monoclinic atomic positions given here and the corresponding triclinic coordinates given by Tanaka *et al.* $\langle U_1 \rangle$ is the atomic displacement (Å) parallel to the longest principal axis of the thermal ellipsoid averaged from the anisotropic displacement parameters of the corresponding split atoms in the triclinic setting.

Atom	Standard name	x	y	z	B_{eq} (Å^2)	Δd (Å)	$\langle U_1 \rangle$ (Å^2)
Si1	Si22b	0.342	0.1485	0.983	0.63	0.035(28)	0.11
Si2	Si12a	0.712	0.035	0.191	0.71	0.028(28)	0.11
Si3	Si22a	0.408	0.126	0.6935	0.64	0.028(28)	0.11
Si4	Si11b	0.022	0.476	0.439	0.56	0.028(28)	0.10
Si5	Si21b	0.3555	0.373	0.961	0.65	0.028(28)	0.11
Si6	Si11a	0.735	0.4985	0.622	0.64	0.036(28)	0.11
Al 1	Al 12b	0.002	0.006	0.0005	0.59	0.028(28)	0.10
Al2	Al21a	0.390	0.3555	0.652	0.62	0.035(28)	0.11
Ca1	Ca1	0.041	0.217	0.4235	1.34	0.028(28)	0.18
O1	O12a	0.1135	0.105	0.954	1.38	0.030(27)	0.17
O2	O62	0.857	0.043	0.0965	1.68	0.043(27)	0.17
O3	O22b	0.193	0.077	0.592	1.36	0.030(27)	0.18
O4	O22a	0.512	0.109	0.1335	1.14	0.032(26)	0.16
O5	O51	0.4285	0.1225	0.8575	1.69	0.036(28)	0.19
O6	O12b	0.617	0.073	0.684	1.10	0.030(27)	0.15
O7	O42	0.8515	0.064	0.355	1.23	0.044(27)	0.17
O8	O31	0.335	0.263	0.000	1.61	0.029(27)	0.18
O9	O32	0.399	0.2325	0.6355	1.16	0.036(27)	0.15
O10	O11a	0.1625	0.4275	0.987	1.13	0.037(27)	0.15
O11	O61	0.831	0.483	0.4965	1.20	0.028(27)	0.16
O12	O21b	0.164	0.383	0.4995	1.22	0.015(27)	0.16
O13	O21a	0.5755	0.411	0.0815	1.30	0.028(28)	0.17
O14	O52	0.355	0.389	0.8065	1.50	0.028(28)	0.17
O15	O11b	0.6195	0.403	0.639	1.36	0.028(28)	0.16
O16	O41	0.9265	0.470	0.267	0.98	0.030(27)	0.13
OW17	OW17	0.986	0.2555	0.1735	5.8	0.022(28)	0.37
OW18	OW18	0.9045	0.2315	0.625	3.0	0.037(27)	0.25
OW19	OW19	0.690	0.2855	0.333	3.4	0.036(28)	0.28
OW20	OW20	0.341	0.147	0.3585	5.5	0.031(26)	0.36

in a comprehensive review by Kahr and McBride (1992), stating that "the optical symmetry of many crystals is lower than would be expected from their external form and X-ray diffraction data".

Conclusion

Using the four criteria established above shows that by none of them can it be considered proven that the v{120} growth sector of yugawaralite has triclinic symmetry. This finding does not touch upon its optically triclinic character. All it means is that the single-crystal XRD structure analysis by Tanaka *et al.* (2002) has not established a triclinic symmetry for the v{120} sample. This is not surprising in the sense that optical observations can be more sensitive to deviations in symmetry than X-ray analyses usually are. Furthermore it is conceivable that in the future a more thorough X-ray analysis could establish a deviation from monoclinic symmetry. As it stands

the best currently available description of the crystal structure of the growth sector v{120} of yugawaralite is obtained in space group *Pc* from an appropriate averaging of the triclinic coordinates reported by Tanaka *et al.* (2002), see Table 1.

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