The *Stella Quadrangula* as a Structure Building Unit

By Harry Nyman and Sten Andersson

Inorganic Chemistry 2, Chemical Center, PO Box 740, S-220 07 Lund, Sweden

Abstract

In order to get a simple and accurate description of complex crystal structures, the *stella quadrangula* is used as a building unit to describe the following structures: SiF_4, scheelite, $NaZn_{13}$, Ru_7B_3 and $Ba_3Fe_3Se_7$.

Introduction

In an earlier paper (Nyman & Andersson, 1979) we used *stella quadrangula*, Fig. 1, or capped versions of it, to describe some rather complex structures. Our belief that this particular unit is of considerable importance in structure building encouraged us to use it for the explanation of other alloy and ionic structures.

SiF_4

Atoji & Lipscomb's (1954) X-ray determination of the crystal structure of SiF_4 provides the following data: Space group $I\bar{4}3m$, $a = 5\cdot41$ Å, 2 Si in 2(*a*) 0,0,0, 8 F in 8(*c*) *x,x,x*, with $x = 0\cdot165$.

This structure (Fig. 2) may be described simply as a cubic array of corner-sharing *stellae quadrangulae* with a Si atom in the central tetrahedron.

If *d* is the edge of a tetrahedron, the calculated unit cell becomes

$$a = d\sqrt{2}/2\left(\sqrt{3}\sin\frac{3}{2}\theta + 1\right)$$

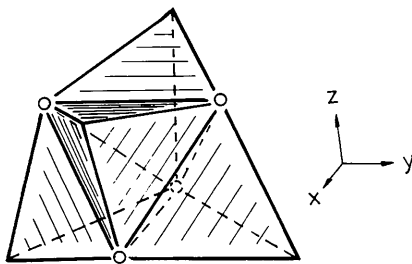$$= d\sqrt{2}/2\left(\frac{5}{3} + 1\right) = 4d\sqrt{2}/3 \simeq 1\cdot886\, d,$$

Fig. 1. A *stella quadrangula*–a tetrahedron capped with four tetrahedra.

where θ, the dihedral angle of a tetrahedron, is $70\cdot533°$.

The position of the corners of the *stella quadrangula* is then given by

$$x = \frac{1}{a}\frac{d}{2\sqrt{2}} = \frac{3}{16} \simeq 0\cdot187.$$

In this model the size and charge of Si^{4+} shrinks the central tetrahedron and consequently the *stella quadrangula* is distorted, but the displacement is rather small $[(0\cdot187 - 0\cdot165)\sqrt{3} \times 5\cdot41 \simeq 0\cdot206$ Å].

$CaWO_4$ (Scheelite)

Many compounds crystallize with the scheelite-type structure, which is tetragonal with c/a from $\sim2\cdot05$ to $\sim2\cdot74$. The broad c/a range indicates that the structure is always more or less distorted. This structure can be described by using W-centered *stellae quadrangulae* which share four edges with four other units (Fig. 3).

Crystal data for $CaWO_4$: Space group $I4_1/a$, $a = 5\cdot243$, $c = 14\cdot376$ Å, $c/a = 2\cdot74$. The O atom position is 16(*f*) *x,y,z*, with $x = 0\cdot2413$, $y = 0\cdot1511$, $z = 0\cdot0861$ (Kay, Frazer & Almodovar, 1964). The structure is plotted in Fig. 4.
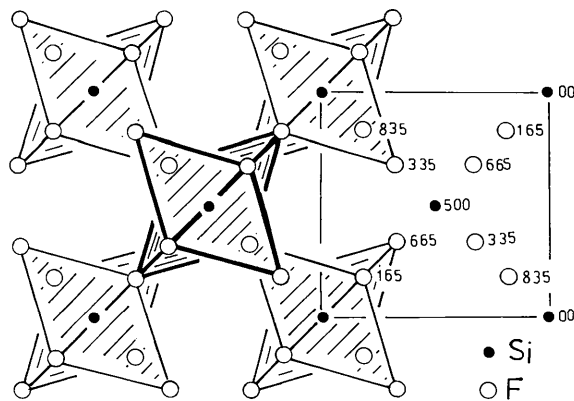

Fig. 2. The structure of SiF_4.

From an ideal framework of *stellae quadrangulae* the structural parameters are

$$a = d\left(3\sin^2\frac{3}{2}\theta + 1\right)^{1/2} = d\left[\left(\frac{5}{3}\right)^2 + 1\right]^{1/2}$$

$$= \frac{d\sqrt{34}}{3} \simeq 1\cdot944d,$$

$$c/a = 1\cdot94,$$

$$c = 4d\sin\theta = d\,8\sqrt{2/3} \simeq 3\cdot771d,$$

where θ is the tetrahedral dihedral angle.

$$x = d\cos\alpha/2a = 0\cdot221; \qquad y = d\sin\alpha/2a = 0\cdot132;$$

$$z = d\sqrt{2}/4c = 0\cdot094; \qquad \sin\alpha = d/a;$$

α is shown in Fig. 3.

When depicted on this model, the structure of LiYbF$_4$ (Thoma, Brunton, Penneman & Keenan, 1969) agrees even more closely than that of CaWO$_4$ with $c/a = 2\cdot06$, $x = 0\cdot2166(6)$, $y = 0\cdot1661(6)$, $z = 0\cdot0814(3)$.

The Ca and Li ions are situated in distorted bis-disphenoids created between the *stellae quadrangulae* as shown in Fig. 4.[*]

NaZn$_{13}$

The crystal structure of NaZn$_{13}$ and several isostructural compounds which were first reported by Ketelaar

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[*] Prior to this publication, Dr Paul M. Skarstad had pointed out to us that the CaWO$_4$ structure can also be derived by using empty edge-sharing tetrahedra. This is in principal the same description.
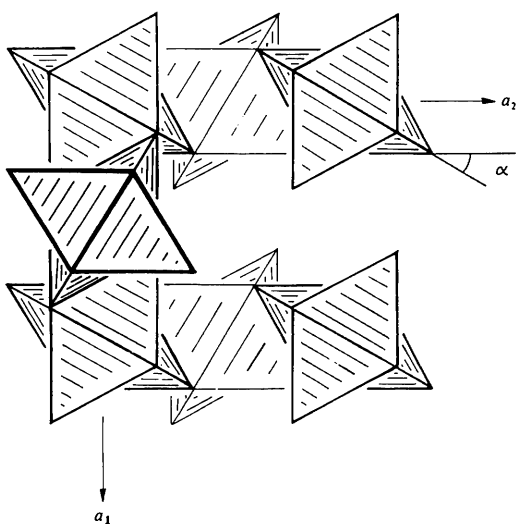
(1937) were later refined by Shoemaker, Marsh, Ewing & Pauling (1952). They describe this structure as face-sharing Na-centered snub cubes of Zn atoms. These snub cubes also share faces with Zn-centered iscosa-hedra of Zn atoms. Neither the snub cubes nor the icosahedra are perfect. However, the structure can also be described in terms of a framework of slightly distorted corner-connected *stellae quadrangulae* which occupy the empty space between the snub cubes and the icosahedra (Fig. 5). This framework cannot be built with ideal *stellae quadrangulae* and Fig. 6 shows one way to distort the *stella quadrangula* unit in order to make it usable in the NaZn$_{13}$ structure. The ideal *stella quadrangula* (full lines) is distorted to a shape indicated by dotted lines when d is rotated an angle α. In this operation c and b_1 are lengthened and b_2 is shortened. When $b_2 = b_1$, which is achieved with $\alpha \simeq 2\cdot45°$, the unit can be used to build the NaZn$_{13}$ structure. A framework of units distorted in that way gives the following parameters:

$$a = 2c_1 + 4h = 2\cdot1192d + 2\cdot4990d = 4\cdot6182d;$$

$$y = 0\cdot1718; z = 0\cdot1147.$$

A model with only ideal snub cubes gives $y = 0\cdot1761$; $z = 0\cdot1141$. These figures may be compared with the Zn position in NaZn$_{13}$ which is 96(i) 0,y,z, of $Fm3c$ with $y = 0\cdot18063$, $z = 0\cdot11924$ (Shoemaker, Marsh, Ewing & Pauling, 1952). A more recent refine-

Fig. 3. The ideal scheelite structure viewed along c. For clarity some of the *stellae quadrangulae* are omitted.
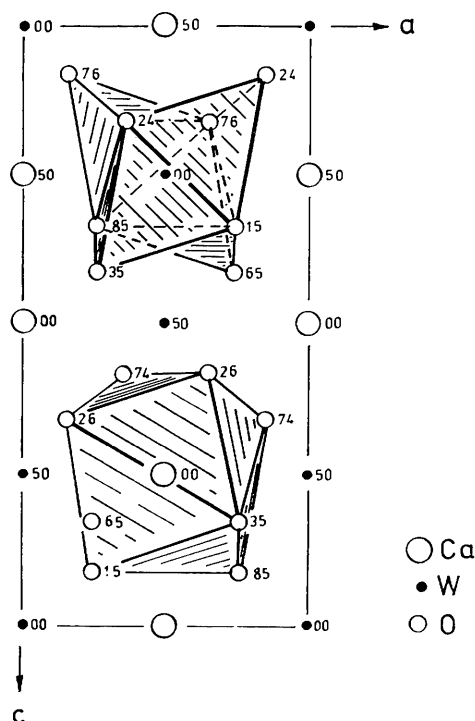

Fig. 4. The structure of CaWO$_4$ seen along a. One *stella quadrangula* is shown and, in the lower part, one Ca-centered distorted bisdisphenoid.

ment of isostructural $MgBe_{13}$ and $CaBe_{13}$ (Baker, 1962) gives parameters as follows:

$$MgBe_{13} \quad y = 0.1789; \quad z = 0.1143;$$
$$CaBe_{13} \quad y = 0.1769; \quad z = 0.1123.$$

Both models are in good agreement with the observed structures, but as shown in Table 1, the size of unit cell and the snub cube is not determined by the large atom centering the snub cube. Instead, the size of the unit cell

Table 1. *Comparison of unit cell and snub cube for several isostructural compounds*

	a (Å)	r_A/r_B
$NaZn_{13}$	12·228	1·40
KZn_{13}	12·360	1·72
$MgBe_{13}$	10·166	1·41
$CaBe_{13}$	10·312	1·74

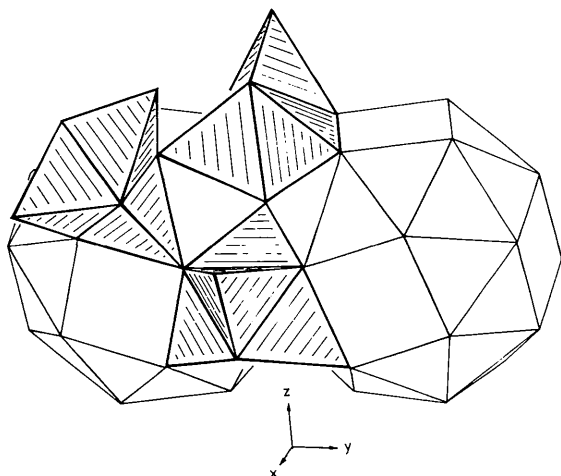r_A/r_B values from Schubert (1964).

Fig. 5. A part of the $NaZn_{13}$ structure, showing two face-sharing snub cubes sharing faces with three corner-connected *stellae quadrangulae*.
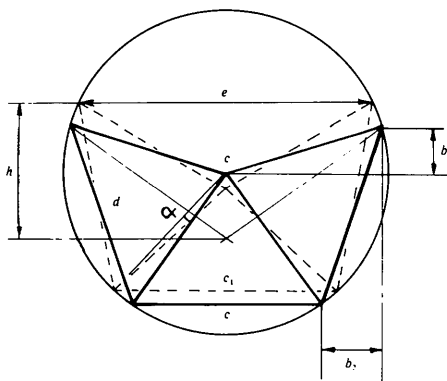

Fig. 6. The distortion of a regular *stella quadrangula* to make it usable as a building element in $NaZn_{13}$. See text.

is determined only by the structure building unit, *viz* the *stella quadrangula*.

Ru_7B_3 and $Ba_3Fe_3Se_7$

$Ba_3Fe_3Se_7$ (Hong & Steinfink, 1972) has essentially the same structure as Ru_7B_3, which is a trilling of h.c.p. or the Fe_3C structure (Aronsson, 1959; Hyde, Bagshaw, Andersson & O'Keeffe, 1974). Se replaces Ru and Ba takes the B position inside a tricapped trigonal prism. The Fe atoms enter the interstices, in this case three out of the four tetrahedra of a *stella quadrangula*. The fourth tetrahedron is slightly elongated and shares faces with three distorted trigonal prisms (Fig. 7). Thus this common structure type can be described by using *stella quadrangula* units. The Fe–Se network of $Ba_3Fe_3Se_7$ can be built of partly capped *stellae quadrangulae* which share corners, Fig. 8. This framework creates interstices in the form of columns of face-sharing empty octahedra running parallel to c, and tricapped trigonal prisms centered with Ba.

There are three different Se positions in the structure. If Se(3) is taken as a fixed point, then the others can be calculated assuming ideal capped *stellae quadrangulae*. Table 2 shows the calculated parameters compared with those given by Hong & Steinfink (1972).
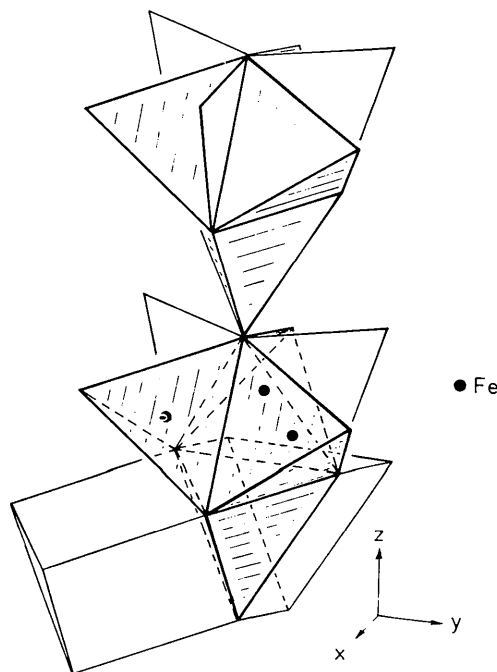

● Fe

Fig. 7. A clinographic projection of a part of the $Ba_3Fe_3Se_7$ structure showing a column of corner-connected partly capped *stellae quadrangulae*. In the lower part of the figure, two of the three surrounding trigonal prisms are shown.

Table 2. *Comparison of observed and calculated parameters of* $Ba_3Fe_3Se_7$

	Calculated			Observed*		
	x	y	z	x	y	z
Se(1)	0·4557	0·9113	0·288	0·4573 (5)	0·9146 (5)	0·3110 (7)
Se(2)	0·1294	0·2588	0·588	0·1252 (4)	0·2504 (4)	0·5895 (7)
Se(3)	1/3	2/3	0·738	1/3	2/3	0·738 (1)

* Hong & Steinfink (1972).

The calculated unit-cell dimensions become

$$a = d(0·9958 + \sqrt{3} + 1) \simeq 2·7247d;$$

$$c = 2d(0·0916 + \sqrt{2}/\sqrt{3}) \simeq 1·8162d;$$

$$c/a = 0·667; \qquad c/a(\text{obs}) = 0·681.$$

The figures in Table 2 show fairly good agreement between the model and the observed structure. However, in the observed structure, the part of the *stella quadrangula* containing Fe is compressed along c, and the part sharing faces with prisms is slightly elongated. This deformation of the *stella quadrangula* leads to elongation of the empty octahedra in the c direction.

On the other hand, Ru_7B_3 is better described by ideal *stella quadrangula* sharing corners with columns of ideal octahedra. Unit-cell dimensions for that structure model are

$$a = d + d\sqrt{3}\,\sin\frac{3}{2}\,\theta = d\left(1 + \frac{5}{3}\right) \simeq 2·6666d;$$

$$c = 2d\,\sqrt{2}/\sqrt{3} \simeq 1·6330d;$$
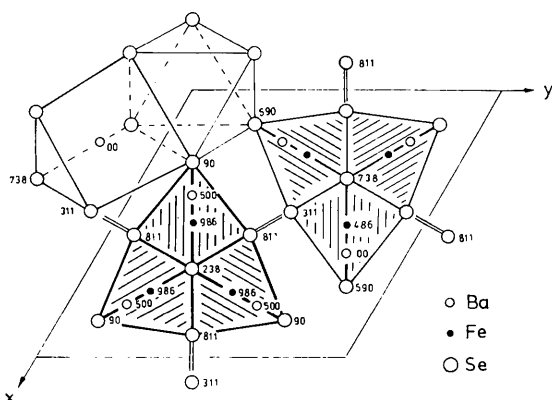
$$c/a = 0·612; \qquad c/a(\text{obs}) = 0·631.$$

Table 3. *Observed and calculated parameters of* Ru_7B_3

	Calculated		Observed	
	x	z	x	z
Ru(1)	0·458	0·318	0·456	0·318
Ru(2)	0·125	0·985	0·122	0·000
Ru(3)	1/3	0·818	1/3	0·818

In Table 3 observed and calculated parameters are given for Ru_7B_3. The agreement for Ru_7B_3 is remarkable; the deviations in x are within the estimated accuracy of the structure determination but in z are significant, although still very small, viz 0·07 Å. Comparing the figures in Tables 2 and 3 shows what might be expected; the alloy (Ru_7B_3) is closer to the ideal structure than is the ionic compound $Ba_3Fe_3Se_7$.

Fig. 8. The structure of $Ba_3Fe_3Se_7$. The double lines indicate how the columns of *stellae quadrangulae* cap each other.

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