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# Aluminate Sodalite Ca$_8$[Al$_{12}$O$_{24}$](WO$_4$)$_2$* at Room Temperature

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**Abstract.** $M_r = 1524{\cdot}1$, orthorhombic, $Aba2$, $a = 26{\cdot}151\ (2)$, $b = 13{\cdot}075\ (1)$, $c = 9{\cdot}319\ (1)$ Å, $V = 3186{\cdot}3\ (8)$ Å$^3$, $Z = 4$, $D_x = 3{\cdot}177$ Mg m$^{-3}$, $F(000) = 2880$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 2{\cdot}638$ mm$^{-1}$, twinned crystal, $R = 0{\cdot}041$ for 2671 independent reflections including 816 detwinned superimposed reflections. The sodalite framework is entirely composed of AlO$_4$ tetrahedra and its partial collapse is anisotropic in contrast to most of the other usually cubic sodalites. The anisotropy can be attributed to interactions between framework oxygens and the WO$_4$ group which is rotated by ~45° about the [001] direction out of the position where its threefold axes match those of the framework. Two reversible phase transitions occur at 614 and 656 K.

**Introduction.** The common feature of all members of the sodalite family is a framework of corner-linked $TO_4$ tetrahedra ($T = $ Si$^{4+}$, Al$^{3+}$, B$^{3+}$, Ga$^{3+}$, Ge$^{4+}$, Be$^{2+}$, ...). It is convenient to subdivide the family according to the $T$ cations; *e.g.* the naturally occurring aluminosilicate sodalites have a framework composition [Al$_6$Si$_6$O$_{24}$]$^{6-}$ and aluminate sodalites are characterized by [Al$_{12}$O$_{24}$]$^{12-}$ frameworks. The $T$ cations occupy the vertices of truncated octahedra which are connected to each other *via* their 4-rings and 6-rings in such a way that the available space is completely filled. The truncated octahedra are often referred to as sodalite cages or, especially in zeolite chemistry, as $\beta$-cages. They accommodate the cage cations and cage anions, both of which exhibit a great variety as to the occurring chemical species. The diversity is limited mainly by the sizes of the cage ions and by the demands on charge compensation for the negatively charged framework.

The framework adapts itself to the sizes and, as will be shown in this and subsequent works, also to the shapes of the cage ions and it is this adaptation which is referred to as 'folding', 'partial collapse' or 'crumpling' of the sodalite framework. The folding is accomplished by cooperative rotations of the $TO_4$ tetrahedra (see, *e.g.*, Fig. 1 of Taylor, 1972). For ideal, cubic sodalites, the tetrahedra rotate about the $\bar{4}$ axes and the amount of the rotation is measured by the so-called tilt angle $\varphi$. This angle has the same absolute value for all tetrahedra and, therefore, one can call this behaviour isotropic folding. The symmetry of the ideal framework is thereby reduced from $Im3m$ to $I\bar{4}3m$ (ordering on the $T$ sites would further reduce the symmetry, as is the case for most of the aluminosilicate sodalites). Hence, $I\bar{4}3m$ is the highest possible symmetry of a partially collapsed sodalite. Well-established geometrical relationships exist between the tilt angle and the lattice parameters, the tetrahedra edge lengths and the fractional coordinates of the framework oxygens (Taylor, 1972; Nyman & Hyde, 1981; Koch & Hellner, 1981). For non-ideal, perhaps non-cubic, sodalites the situation is more complicated since there is no longer one single tilt angle for the whole framework, but individual tetrahedra have to be considered. New concepts for a description of the folding in those cases had, therefore, to be developed. This has been done for the group of aluminate sodalites, for which the term 'anisotropic folding' has been used (Depmeier, 1983). A method to describe the anisotropic folding quantitatively will be published elsewhere (Depmeier, to be published).

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* Hexaaluminium tetracalcium dodecaoxide tungstate.

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In the beginning, aluminate sodalites raised our interest (Saalfeld & Depmeier, 1972; Depmeier, 1971) because these compounds possess necessarily $AlO_4$ tetrahedra which are connected to each other and whose existence is, therefore, to a certain extent in conflict with Loewenstein's (1954) aluminium avoidance rule. In addition, the temperature necessary for the preparation by sintering ($\sim 1623$ K) marked an unusually high thermal stability of these zeolite-like materials. The interest increased when we observed on Guinier films splitting of reflections and, for several aluminate sodalites, the occurrence of superstructure reflections (Saalfeld & Depmeier, 1972; Depmeier, 1979). These observations clearly indicated a symmetry lower than cubic and/or unit-cell parameters larger than the usual $\sim 9$ Å. Moreover, both observations strongly suggested the existence of phase transitions. Indeed, DSC (differential scanning calorimetry) and optical measurements could establish the existence of reversible phase transitions for all aluminate sodalites with tetrahedral cage anions (Depmeier, 1979). The transition temperatures have been found to lie between $\sim 300$ K and $\sim 700$ K (and are easily shifted by making mixed crystals).

Certain analogies with the boracite family (Schmid, 1965) led us to expect that interesting ferroic properties could be connected with the phase transitions. This is the reason why we have begun a programme to study the preparation, the structures and the properties of aluminate sodalites. This is the first structural report in the frame of this research programme;* others will follow as the work proceeds.

**Experimental.** *Crystal preparation and data collection.* Sintered material of Ca-$WO_4$ aluminate sodalite $\{Ca_8[Al_{12}O_{24}](WO_4)_2$, hereinafter abbreviated CAW$\}$ has been prepared as described by Saalfeld & Depmeier (1972). Pellets of sintered CAW were partially melted in an iridium crucible placed in a high-frequency furnace. No temperature control could be made, but the fusion could be observed well. After rapid resolidification a mixture of a crystalline mass and unfused pellets was found from which irregularly shaped crystals could be obtained.† The crystals were examined by single-crystal X-ray diffraction, temperature-dependent X-ray diffraction with polycrystalline samples, differential scanning calorimetry and by optical methods using a polarizing microscope equipped with a hot stage. The single-crystal X-ray work confirmed the identity of the crystals and by the latter three techniques the phase transitions could be observed; transitions occur at 614 and 656 K.

Data collection: irregularly shaped crystal, approximately 0·15 mm ∅, Philips PW1100 diffractometer, graphite monochromator, one octant ($h,k,l \geq 0$), $(\sin\theta/\lambda)_{\max} = 0{\cdot}8226$ Å$^{-1}$ ($= 0{\cdot}7035$ for $l > 8$), $\omega$–$2\theta$ scans, scan width $= 0{\cdot}80° + 0{\cdot}10°\tan\theta$, scan speed $0{\cdot}06°\text{s}^{-1}$, background measured on both sides of the reflection with half the scan time used for the peak, three standard reflections after every 120 min (no significant change), 12536 reflections, Lorentz and polarization corrections, no absorption correction ($\mu R \sim 0{\cdot}2$); lattice parameters from a least-squares fit to the centred angles of 33 reflections with $8{\cdot}7° \leq 2\theta \leq 38{\cdot}1°$. Due to arguments which are elucidated in the *Twinning* section, the value of $b$ (see *Abstract*) had to be halved compared to the value which was used for the data collection. An additional 2675 possible superstructure reflections were measured in order to clarify whether a doubling of the $c$ parameter was required, as had been assumed from powder work in Depmeier (1979). No unambiguous deviation from zero intensity could be detected.

*Pseudomerohedral twinning, space-group determination and detwinning.* The data collection as described above yielded an orientation matrix based on a $\sim 26 \times 26 \times 9$ Å unit cell which corresponded to that of an apparently tetragonal single crystal used in Depmeier (1979); the intensity distribution, however, was clearly orthorhombic. In the meantime, several new crystals had been tested by film techniques and violations of tetragonal symmetry had been observed, too. The ratio of intensities of reflections $hkl$ and $khl$ varied from crystal to crystal and it was at this point that it became evident that a twin problem was present. The observed intensity distribution was compatible with twin planes (110) or ($\bar{1}10$). On 'single-crystal' photographs of the twinned crystals no splitting of reflections could be observed. Therefore, the twinning operation cannot transform $c_i$ into $a_j$ or $b_j$ (indices $i$ and $j$ refer to the $i$th and $j$th twin individual, respectively), because $c$(pseudocubic) and $a$(pseudocubic) or $b$(pseudocubic) have different lengths. Hence, the twin planes must be parallel to $c$.

The superposition of the reciprocal lattices of the two twin domains yielded 'non-crystallographic' systematic extinctions (see Depmeier, 1979) which made it impossible to deduce directly the true space group of CAW. However, it could be found making use of the following conditions. Firstly, it was assumed that the phase transitions occurring in CAW reduce the symmetry. If this is true, the tables of Neubüser & Wondratschek (1970, 1977) can be used. Secondly, because of the orthorhombic intensity distribution of the twinned crystals, the resulting space group must be at most orthorhombic. In addition, it should be non-centrosymmetric, because the highest possible symmetry of a partially collapsed cubic sodalite is $I\bar{4}3m$. Thirdly, the systematic extinctions of the real space group, operated on by the twinning, should give

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[*] Preliminary results have been reported at the 22. Diskussionstagung der Arbeitsgemeinschaft Kristallographie, Kiel, 1982 and in *Progress Reports for the Swiss National Science Foundation.*

[†] In the meantime, we have developed methods of growing crystals of the majority of aluminate sodalites by the flux technique.

the observed extinctions of the twinned crystal. The symmetry reduction implies changes of the unit-cell translations. The procedure resulted in space group $Aba2$ with basic vectors $2\sqrt{2}a_{ps}$, $\sqrt{2}a_{ps}$, $c_{ps}$ ($a_{ps}$, $c_{ps}$ are here pseudocubic ~9 Å lattice parameters). The transformation matrix for cubic → orthorhombic axes is $(2\bar{2}0,110,001)$. Fig. 1 shows the symmetry reduction starting from the space group of the aristotype (Megaw, 1973). The sequence shown need not necessarily correspond to the actual symmetry reduction and further experimental results are needed to confirm or to reject the proposed sequence. Optical observations, however, confirm the general features of this sequence. The 656 K phase transition is characterized by the occurrence (on heating) of optical isotropy, thus indicating that the high-temperature phase is, indeed, cubic. The transition at 614 K is accompanied by a marked discontinuity of the birefringence. This behaviour makes it highly probable that the symmetry of the intermediate phase is tetragonal.

In the foregoing the twin operation had been identified as being mirror planes parallel to the pseudotetragonal (~26 × 26 × 9 Å) planes (110) and $(\bar{1}10)$. The actual size of the unit cell with $b$ being halved makes the indices of the twin planes (210) and $(\bar{2}10)$.

Since $|a| = 2|b|$, the twinning results in apparently equivalent axes $a' = b'$ and, therefore, in apparent tetragonal symmetry, provided that the intensity contributions of the two individuals are equal. The metric relationship between $a$ and $b$ explains also the observation that on powder photographs no orthorhombic splitting is observed, consequently, they have a tetragonal aspect.*

The fact that in CAW a part of the reciprocal-lattice points of both twin individuals coincides (whilst the remaining points of each reciprocal lattice fall on empty points of the other reciprocal lattice) is reminiscent of what is found when twinning by merohedry occurs. Klapper & Hahn (1979) distinguished two types of merohedral twinning, the subdivision depending on whether or not the twin element was a symmetry element of the Laue class of the crystal. In any case of true merohedral twinning, however, the twin element belongs to the holohedral class. In our case the twin elements have been identified to be mirror planes with indices (210) and $(\bar{2}10)$ for the orthorhombic unit cell. Hence, the twinning of CAW certainly cannot be called merohedral. However, the symmetry reduction requires two steps with a ~9 × 9 × 9 Å unit cell, *viz.* the supposed aristotype with point symmetry $\bar{4}3m$ and its tetragonal subgroup $\bar{4}2m$. In both cases the observed twin elements have the indices (100) and (010) and they are symmetry elements of both, the Laue class and the holohedry ($m3m$ and $4/mmm$, respectively; Laue class and holohedry are identical in both cases). In CAW we are, therefore, faced with merohedral twinning of the pseudosymmetry and the twinning may, therefore, be qualified as pseudomerohedral.

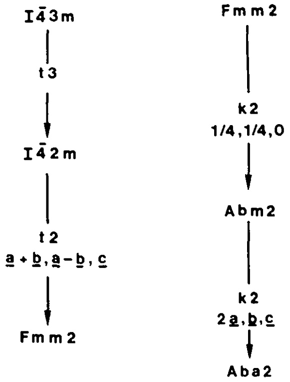

Fig. 1. The proposed symmetry reduction *via* smallest steps of maximal subgroups from the hypothetical high-temperature phase of CAW with space group $I\bar{4}3m$ to the room-temperature phase with space group $Aba2$. The index of the group–subgroup relationships is given as well as its type, *viz. t* for *translationengleich* and *k* for *klassengleich*. Unit-cell transformations and a shift of the origin are also indicated.

Having established that the crystal was twinned, it was desirable to reduce the data set to reflections coming from one twin individual only. It was decided to keep reflections with $k = 4n$ (for $l$ even) and $k = 4n + 2$ (for $l$ odd). Since these $k$ indices referred to the pseudotetragonal ~26 × 26 × 9 Å unit cell, they had to be halved in order to be in accordance with the $A$-centred orthorhombic cell. However, not all reflections obtained in this way originated exclusively from one twin individual. Taking into account the twin law, the relationship $|a| = 2|b|$ and the systematic extinctions due to the $A$-centring the intensity of $\frac{1}{4}$ of these reflections was still composed of contributions from both kinds of twin domains. This concerned those reflections which obeyed the conditions $l$ even: $h = 4n$ or $l$ odd: $h = 4n + 2$. In a first approach it was then possible to eliminate the superimposed reflections and to start the structure determination and a preliminary refinement by using only the reflections from the chosen twin individual. In order to avoid a biased data set, however, the superimposed reflections had to be detwinned and included in the refinement. This detwinning proceeded as follows. Let $I(hkl)$ and $I(khl)$ be the intensities of superimposed reflections, where indices $hkl$ refer to the ~26 × 26 × 9 Å cell and the twin law is (110). The intensity contributions of the individuals are $J(hkl)_1$, $J(khl)_1$, $J(hkl)_2$ and $J(khl)_2$, where subscripts 1 and 2 denote the individuals with the larger and smaller volume, respectively. α is the volume fraction of the smaller twin individual. We then find that

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* In the powder work of Depmeier (1979) the reflections had been indexed corresponding to a tetragonal unit cell. In view of the single-crystal results of this work, the indices given there have to be transformed with $(100,0\frac{1}{2}0,00\frac{1}{2})$.

$$I(hkl) = J(hkl)_1 + J(khl)_2 = J(hkl)_1 + \frac{\alpha}{(1-\alpha)} J(khl)_1 \quad (1)$$

and

$$I(khl) = J(khl)_1 + J(hkl)_2 = J(khl)_1 + \frac{\alpha}{(1-\alpha)} J(hkl)_1. \quad (2)$$

Substituting and reordering gives

$$J(khl)_1 = \frac{(1-\alpha)^2}{(1-2\alpha)} I(khl) - \frac{\alpha(1-\alpha)}{(1-2\alpha)} I(hkl) \quad (3)$$

and

$$J(hkl)_1 = I(hkl) - \frac{\alpha}{(1-\alpha)} J(khl)_1. \quad (4)$$

If α is known and if it is sufficiently distinct from 0·5, equations (3) and (4) allow the calculation of the untwinned intensities. Similar formulae for detwinning have been used earlier (Britton, 1972). α can be determined from the ratio $I(hkl)/[I(hkl) + I(khl)]$, if one of the two contributions $J(hkl)$ or $J(khl)$ is accidently zero. Listing those ratios for a sufficiently high number of reflections, a lower limit can be found which gives α. For CAW, this method gave to a good approximation $\alpha = 0{\cdot}25$. A different method for determining α has recently been proposed by van Koningsveld (1983). With $\alpha = 0{\cdot}25$ and using equations (3) and (4), a total of 816 superimposed reflections has been detwinned and included in the data set which then contained a total of 2932 independent reflections, 2547 of which had $J > 3\sigma(J)$ and were classed as observed.

*Structure refinement.* X-ray evidence made it clear from the beginning that CAW belonged to the sodalite family. Therefore, the transformed coordinates of cubic, natural sodalite (Löns & Schulz, 1967) were chosen as a starting point. Alternating cycles of least-squares refinements and Fourier syntheses allowed the location of all atoms, including the $WO_4$ oxygens. The function minimized in a blocked least-squares refinement was $\sum w(|F_o|-|F_c|)^2$; scattering factors were for neutral atoms; 244 variables included one scale factor and 79 positional and 164 anisotropic thermal parameters of 28 independent atoms. With 2671 reflections having $F_o > 10{\cdot}0$ and a weighting scheme which discriminated mainly against detwinned reflections ($w = xy$, with $x = \sin\theta/0{\cdot}3$ if $0{\cdot}3 > \sin\theta$, otherwise $x = 1$; $y = 1$ for $F_o < 375$, otherwise $y = 375/F_o$; $w = 0$, if $0{\cdot}9F_o > F_c$), final $R$ and $wR$ were both 0·041.* $(\Delta/\sigma)_{\rm ave} = 0{\cdot}048$. A difference Fourier map calculated after the final least-squares cycle showed only minor residual peaks around the W atom.

Since the degree of occupation of the cages by cations and anions is variable, the population parameters of the Ca atoms, of W and of the tungstate oxygens were allowed to vary independently together with the other parameters. The result showed no significant deviation from 1·0 for any of them and, therefore, we must conclude that the cages in CAW are fully occupied. This is in contrast to what has been found for nosean (Schulz, 1964, 1970; Schulz & Saalfeld, 1965; Löns, 1969) and for haüyne (Saalfeld, 1961; Löhn & Schulz, 1968), both of which are naturally occurring aluminosilicate sodalites containing tetrahedral cage anions.

All calculations were performed with the XRAY76 system of programs (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a Univac 1100 computer.

**Discussion.** Table 1 lists the final positional parameters and equivalent isotropic temperature factors, Table 2 the bond distances and angles as well as the non-bonding O···O distances for the $AlO_4$ and $WO_4$ tetrahedra and Table 3 contains the most important bond distances within the coordination spheres of the Ca cage cations.

CAW has, indeed, all the structural characteristics of the sodalite family: its framework is built up from the $AlO_4$ tetrahedra, the cage cations lie close to the 6-rings of the framework and the cage anion occupies the centre of the cages. However, there are remarkable distortions of some of the primary building units ($AlO_4$

Table 1. *Fractional atomic coordinates* (× $10^4$, × $10^5$ *for* W) *and equivalent isotropic thermal parameters* (Å$^2$, × $10^3$)

E.s.d.'s are in parentheses. $U_{eq}$ = 1/3 trace **U**.

| | Wyckoff notation | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|
| Al(1) | 8(*b*) | 1853 (1) | −1243 (2) | 9 (5) | 7 (1) |
| Al(2) | 8(*b*) | 4369 (1) | 1134 (2) | −236 (3) | 6 (1) |
| Al(3) | 8(*b*) | 3101 (1) | 1253 (2) | 138 (4) | 5 (1) |
| Al(4) | 8(*b*) | 4403 (1) | 3652 (2) | −46 (4) | 7 (1) |
| Al(5) | 8(*b*) | 2569 (1) | 24 (2) | 2585 (4) | 5 (1) |
| Al(6) | 4(*a*) | 0 | 0 | 2283 (4) | 7 (1) |
| Al(7) | 4(*a*) | 5000 | 0 | 2443 (5) | 6 (1) |
| Ca(1) | 8(*b*) | −1381 (1) | 234 (2) | 2784 (2) | 14 (1) |
| Ca(2) | 8(*b*) | −1202 (1) | 4880 (2) | 2460 (3) | 13 (1) |
| Ca(3) | 8(*b*) | 167 (1) | 2669 (1) | 2028 (2) | 11 (1) |
| Ca(4) | 8(*b*) | 2499 (2) | 2604 (1) | 2490 (4) | 10 (1) |
| O(1) | 8(*b*) | −1265 (2) | 4138 (5) | 140 (11) | 10 (2) |
| O(2) | 8(*b*) | 1218 (2) | 3947 (6) | 5485 (8) | 11 (2) |
| O(3) | 8(*b*) | −174 (3) | 1119 (5) | 1353 (8) | 10 (2) |
| O(4) | 8(*b*) | 2922 (3) | 1038 (5) | 1899 (7) | 9 (2) |
| O(5) | 8(*b*) | 4666 (3) | 886 (5) | 1418 (8) | 11 (2) |
| O(6) | 8(*b*) | 2190 (2) | −736 (5) | 1443 (8) | 10 (2) |
| O(7) | 8(*b*) | 4542 (3) | 2399 (5) | −627 (8) | 12 (2) |
| O(8) | 8(*b*) | 2907 (3) | 2509 (5) | −187 (7) | 9 (2) |
| O(9) | 8(*b*) | 4539 (3) | −700 (5) | 3342 (7) | 9 (2) |
| O(10) | 8(*b*) | 2867 (3) | 5496 (6) | 3771 (8) | 12 (2) |
| O(11) | 8(*b*) | −541 (3) | −368 (6) | 3272 (8) | 13 (2) |
| O(12) | 8(*b*) | 1959 (2) | 4208 (5) | 3235 (7) | 8 (2) |
| O(13) | 8(*b*) | −1046 (4) | 3610 (9) | 4149 (12) | 33 (3) |
| O(14) | 8(*b*) | −1714 (3) | 1854 (6) | 3757 (10) | 20 (2) |
| O(15) | 8(*b*) | −902 (4) | 1784 (8) | 5843 (13) | 33 (3) |
| O(16) | 8(*b*) | −1779 (4) | 3096 (8) | 6319 (12) | 31 (3) |
| W | 8(*b*) | 13626 (1) | 23971 (2) | 0 | 12 (1) |

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* Lists of structure factors, anisotropic thermal parameters and results on bond-valence calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38811 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

tetrahedra, $WO_4$ tetrahedron, $Ca_8$ polyhedra) and of the secondary structure (the sodalite framework, the network of $Ca_8$ polyhedra, the coordination spheres of Ca). It is not the purpose of this paper to deal with these distortions, because they will be the subject of detailed discussions, the results of which will be published elsewhere (Depmeier, to be published).

Table 2. *The geometry of the* $AlO_4$ *and* $WO_4$ *tetrahedra including the distortion parameters BLDP and ELDP* (*Griffen & Ribbe*, 1979)

| | | | | α | d(O···O) |
|---|---|---|---|---|---|
| Al(1)–O(6) | 1·733 (8) Å | O(6)–Al(1)– | O(2) | 103·5 (4)° | 2·726 (9) Å |
| O(2) | 1·737 (7) | O(6) | O(12) | 120·7 (3) | 3·050 (10) |
| O(12) | 1·777 (8) | O(6) | O(8) | 104·7 (4) | 2·764 (9) |
| O(8) | 1·758 (7) | O(2) | O(12) | 109·9 (4) | 2·876 (10) |
| | | O(2) | O(8) | 120·1 (3) | 3·027 (9) |
| | | O(12) | O(8) | 99·0 (4) | 2·687 (9) |

Mean: 1·751 (0·02) Å, BLDP: 0·0116 Mean: 2·855 (0·16) Å, ELDP: 0·0545

| | | | | α | d(O···O) |
|---|---|---|---|---|---|
| Al(2)–O(7) | 1·754 (7) Å | O(7)–Al(2)– | O(5) | 104·0 (3)° | 2·766 (10) Å |
| O(5) | 1·756 (8) | O(7) | O(1) | 118·9 (3) | 3·001 (9) |
| O(1) | 1·731 (6) | O(7) | O(11) | 110·1 (4) | 2·856 (10) |
| O(11) | 1·729 (8) | O(5) | O(1) | 102·0 (4) | 2·710 (10) |
| | | O(5) | O(11) | 122·6 (4) | 3·057 (10) |
| | | O(1) | O(11) | 100·1 (4) | 2·653 (11) |

Mean: 1·743 (0·01) Å, BLDP: 0·0083 Mean: 2·841 (0·16) Å, ELDP: 0·0569

| | | | | α | d(O···O) |
|---|---|---|---|---|---|
| Al(3)–O(8) | 1·745 (7) Å | O(8)–Al(3)– | O(4) | 103·9 (3)° | 2·735 (9) Å |
| O(4) | 1·729 (8) | O(8) | O(10) | 108·0 (4) | 2·808 (10) |
| O(10) | 1·726 (8) | O(8) | O(1) | 123·7 (3) | 3·068 (9) |
| O(1) | 1·735 (6) | O(4) | O(10) | 120·8 (4) | 3·003 (10) |
| | | O(4) | O(1) | 102·1 (4) | 2·694 (10) |
| | | O(10) | O(1) | 99·8 (4) | 2·648 (10) |

Mean: 1·734 (0·01) Å, BLDP: 0·0048 Mean: 2·826 (0·17) Å, ELDP: 0·0608

| | | | | α | d(O···O) |
|---|---|---|---|---|---|
| Al(4)–O(7) | 1·763 (7) Å | O(7)–Al(4)– | O(9) | 98·3 (4)° | 2·665 (10) Å |
| O(9) | 1·761 (8) | O(7) | O(2) | 119·0 (4) | 3·020 (10) |
| O(2) | 1·741 (7) | O(7) | O(3) | 105·1 (4) | 2·777 (10) |
| O(3) | 1·736 (8) | O(9) | O(2) | 108·9 (4) | 2·849 (10) |
| | | O(9) | O(3) | 115·4 (3) | 2·956 (10) |
| | | O(2) | O(3) | 110·1 (4) | 2·849 (9) |

Mean: 1·750 (0·01) Å, BLDP: 0·0079 Mean: 2·853 (0·13) Å, ELDP: 0·0442

| | | | | α | d(O···O) |
|---|---|---|---|---|---|
| Al(5)–O(4) | 1·737 (7) Å | O(4)–Al(5)– | O(6) | 120·5 (4)° | 3·037 (9) Å |
| O(6) | 1·761 (8) | O(4) | O(10) | 108·6 (4) | 2·793 (10) |
| O(10) | 1·702 (8) | O(4) | O(12) | 102·6 (3) | 2·715 (9) |
| O(12) | 1·741 (7) | O(6) | O(10) | 102·7 (3) | 2·706 (11) |
| | | O(6) | O(12) | 105·3 (3) | 2·783 (9) |
| | | O(10) | O(12) | 118·0 (4) | 2·952 (10) |

Mean: 1·735 (0·02) Å, BLDP: 0·0141 Mean: 2·824 (0·14) Å, ELDP: 0·0490

| | | | | α | d(O···O) |
|---|---|---|---|---|---|
| Al(6)–O(3) | 1·760 (7) Å | O(3)–Al(6)– | O(11) | 106·1 (3)° | 2·810 (10) Å |
| O(11) | 1·755 (7) | O(3) | O(3)′ | 121·0 (4) | 3·063 (10) |
| O(3)′ | 1·760 (7) | O(3) | O(11)′ | 103·8 (3) | 2·767 (10) |
| O(11)′ | 1·755 (7) | O(11) | O(3)′ | 103·8 (3) | 2·767 (10) |
| | | O(11) | O(11)′ | 116·6 (4) | 2·988 (10) |
| | | O(3)′ | O(11)′ | 106·1 (3) | 2·810 (10) |

Mean: 1·758 (0·003) Å, BLDP: 0·0017 Mean: 2·868 (0·13) Å, ELDP: 0·0440

| | | | | α | d(O···O) |
|---|---|---|---|---|---|
| Al(7)–O(5) | 1·737 (7) Å | O(5)–Al(7)– | O(9) | 105·5 (3)° | 2·761 (10) Å |
| O(9) | 1·730 (7) | O(5) | O(5)′ | 113·3 (4) | 2·903 (10) |
| O(5)′ | 1·737 (7) | O(5) | O(9)′ | 105·3 (3) | 2·757 (10) |
| O(9)′ | 1·730 (7) | O(9) | O(5)′ | 105·3 (3) | 2·757 (10) |
| | | O(9) | O(9)′ | 122·1 (4) | 3·028 (10) |
| | | O(5)′ | O(9)′ | 105·5 (3) | 2·761 (10) |

Mean: 1·734 (0·004) Å, BLDP: 0·0024 Mean: 2·828 (0·11) Å, ELDP: 0·0402

| | | | |
|---|---|---|---|
| Mean d(Al–O): | 1·743 (0·016) Å | Mean BLDP: | 0·007 (5) |
| Mean d(O···O): | 2·842 (0·133) Å | Mean ELDP: | 0·050 (8) |
| Mean of small angles: | 104·6 (3·2)° | Mean of large angles: | 119·5 (2·9)° |

| | | | | | |
|---|---|---|---|---|---|
| W–O(13) | 1·75 (1) Å | O(13)–W– | O(14) | 111·5 (5)° | 2·91 (1) Å |
| O(14) | 1·77 (1) | O(13) | O(15) | 109·3 (5) | 2·89 (2) |
| O(15) | 1·79 (1) | O(13) | O(16) | 109·5 (5) | 2·87 (2) |
| O(16) | 1·76 (1) | O(14) | O(15) | 107·7 (4) | 2·88 (1) |
| | | O(14) | O(16) | 109·7 (5) | 2·89 (1) |
| | | O(15) | O(16) | 109·1 (5) | 2·90 (2) |

Mean: 1·768 Å, BLDP: 0·010 Mean: 2·89 Å, ELDP: 0·002

Table 3. *The most important calcium–oxygen distances*

| | | | |
|---|---|---|---|
| Ca(1)–O(2) | 2·434 (8) Å | Ca(3)–O(3) | 2·301 (7) Å |
| –O(10) | 2·371 (7) | –O(5) | 2·368 (7) |
| –O(11) | 2·378 (7) | –O(7) | 2·341 (8) |
| –O(14) | 2·463 (9) | –O(15) | 2·33 (1) |
| –O(6) | 2·542 (7) | –O(9) | 2·577 (7) |
| –O(1) | 2·64 (1) | –O(7)′ | 2·966 (8) |
| Ca(2)–O(1) | 2·38 (1) | Ca(4)–O(4) | 2·393 (7) |
| –O(9) | 2·360 (7) | –O(6) | 2·515 (7) |
| –O(12) | 2·423 (7) | –O(8) | 2·413 (8) |
| –O(13) | 2·32 (1) | –O(14) | 2·48 (1) |
| –O(4) | 2·640 (7) | –O(16)′ | 2·36 (1) |
| –O(5) | 2·663 (7) | –O(8)′ | 2·717 (8) |
| | | –O(12) | 2·621 (7) |

The structure of CAW contains seven independent $AlO_4$ tetrahedra. The mean bond length Al–O is 1·74 (2) Å, which is in good agreement with the grand mean value of the Al–O bonds in all-corner connected $TO_4$ tetrahedra (1·75 Å, Griffen & Ribbe, 1979). Two sets of angles (O–Al–O), *viz.* small ones with a mean value of 105 (3)° and large ones with a mean value of 120 (3)°, indicate a strong distortion of the $AlO_4$ tetrahedra.

There is only one independent $WO_4$ group in the structure. No marked tendency to a specific distortion can be observed. This is in contrast to scheelite, $CaWO_4$, where the bond angles indicate a tetragonal distortion of the $WO_4$ tetrahedron (Kay, Frazer & Almodovar, 1964).

It is surprising that the $WO_4$ tetrahedra are oriented in such a way that their (not perfect) threefold axes do not coincide with the latent threefold axes of the framework. They are rather rotated about the [001] direction by about 45°. The sense of rotation is the same for all tetrahedra within rows (in projection) parallel to the *b* axis. In the direction of the *a* axis the tetrahedra of two successive rows have the same orientation, whereupon the sense of the rotation changes and the tetrahedra of the following two rows have the opposite orientation (Fig. 2). Minor rotations occur also about the [100] directions. The relative position of each $WO_4$ tetrahedron with respect to the surrounding $Ca_8$ distorted cube is such that their vertices point to mid-edges rather than to Ca atoms at the corners (such a relation would be expected for an ordered cubic phase). Conversely, the Ca atoms face neither vertices nor faces of neighbouring $WO_4$ tetrahedra.

As frequently encountered, the coordination sphere of Ca by oxygen is not regular (Table 3). Each of the four symmetrically independent Ca atoms is situated close to, but not at, the centre of a 6-ring of the sodalite framework. Three of the six ring oxygens make short bonds (< 2·52 Å) with the Ca atom, the remainder have distances between fairly strong bonds (~2·54 Å) and non-bonded distances. In addition, each Ca is bonded to either one [Ca(1), Ca(2), Ca(3)], or two $WO_4$ oxygens [Ca(4)].

The rotation of the $WO_4$ tetrahedra out of their 'cubic positions' has consequences also for the sodalite framework of $AlO_4$ tetrahedra. The oxygens at the vertices of the $WO_4$ tetrahedra point no longer to the centres of the framework 6-rings, but turn more or less directly towards *some* of the framework oxygens, thereby pushing back the latter. This interaction between framework oxygens and $WO_4$ oxygens gives rise to anisotropic partial collapse and to the formation of a hitherto, at least for sodalites, unknown type of distortion. It may be seen in the 4-ring of $AlO_4$ tetrahedra in the centre of Fig. 3. The figure strongly suggests that the reason for this kind of distortion is the existence of shearing forces and since it affects the conformation of the framework, we wish to call it 'conformational shearing'. It partly replaces the tilting in the total amount of folding of the framework.

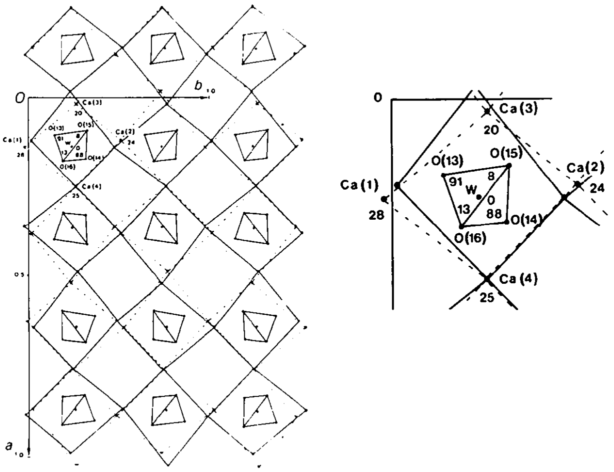

Fig. 2. Projection of the cage ions of CAW onto the *ab* plane showing the orientation of the $WO_4$ groups with respect to the cation network. *z* coordinates (see enlarged inset) are multiplied by 100 and given as integers. W atoms are at heights 0·00 and 0·50 and occupy the centres of the tetrahedra formed by the $WO_4$ oxygens O(13), O(14), O(15) and O(16). The Ca atoms form a framework of corner-connected distorted cubes with Ca(1) at heights 0·28 and 0·78, Ca(2) at 0·24 and 0·74, Ca(3) at 0·20 and 0·70 and Ca(4) at 0·25 and 0·75. The environment of Ca(4) is different from all other Ca atoms.

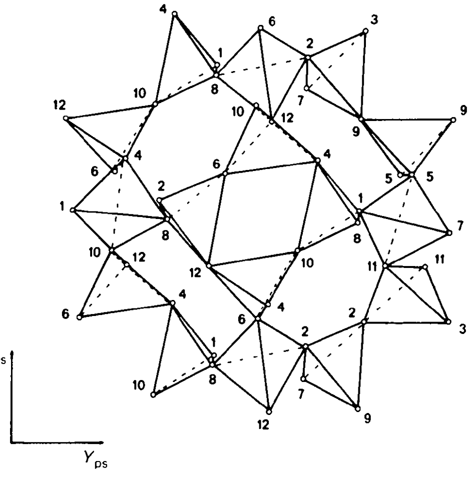

Fig. 3. Projection of a sodalite cage of CAW along the pseudocubic |100| direction. Only framework oxygens are shown; atoms can be identified by the atom numbering given as integers. At the centre one notices a 4-ring which is strongly distorted by conformational shearing and which appears as a rhomb. For pure tilting, the 4-ring would appear rather as a square in the projection.

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