

The e.s.d. of position calculated from full-matrix least squares with space group *Cc* show that some of the atoms have highly significant deviations from the higher symmetry, indicating that *Cc* is correct.

In cases where the space group is not absolutely certain, from a structural point of view it is safest (and cannot be wrong) to assume the lower symmetry. It is my view that the structure of dibenzyl disulphide is adequately described by *Cc*.

Acta Cryst. (1971). B27, 848

Refinement of the structure of γ -Ca₂SiO₄. By REINHARD CZAYA, *Mineralogisches Institut der Universität Kiel, Kiel, Olshausenstrasse, Germany (BRD)*

(Received 26 May 1970)

The crystal structure of γ -Ca₂SiO₄ has been redetermined on the basis of 1198 three-dimensional integrated Weissenberg reflexions. Single crystals of γ -Ca₂SiO₄ were obtained by thermal decomposition of the new compound Ca₂SiO₄·CaCl₂. The results confirm the structure reported by Smith, Majumdar & Ordway, but show that the distortion of the SiO₄ tetrahedron found by these authors is not real.

The structure determination of γ -Ca₂SiO₄ by Smith, Majumdar & Ordway (1963) showed a surprisingly irregular SiO₄ tetrahedron, which is unusual for orthosilicates. Si—O bond lengths range from 1.589 to 1.725 Å. An interpretation of this result could not be given, so that a re-determination of the structure seemed to be necessary.

Single crystals of γ -Ca₂SiO₄ were obtained by thermal decomposition of the synthetic compound Ca₂SiO₄·CaCl₂ (Czaya, 1970). The refined lattice constants (from 43 Guinier reflexions) are:

$$\begin{aligned} a_0 &= 5.078 \pm 0.002 \text{ \AA} \\ b_0 &= 11.225 \pm 0.003 \\ c_0 &= 6.760 \pm 0.002 \end{aligned}$$

These values differ substantially from those given by Smith *et al.* (1963), but are in good agreement with the data given by Yannaquis (1955) and by Yamaguchi, Ono, Kawamura & Soda (1963). Of the possible space groups *Pbnm* and *Pna*₂₁ the former, which is centrosymmetric, proved to be correct.

Integrating Weissenberg photographs for the *hk0* to *hk6* layers were obtained using Mo *K* α radiation, and the intensities of 1198 independent reflexions were measured photometrically. No corrections were made for absorption or extinction. Six cycles of least-squares refinement (full-matrix program) with individual isotropic temperature factors gave an *R* value of 0.07.

Table 1 lists the atomic coordinates and temperature factors and Table 2 gives the interatomic distances and angles.

References

- DIJK, B. VAN & VISSER, G. J. (1971). *Acta Cryst.* B27, 846.
EINSPAHR, H. & DONOHUE, J. (1971). *Acta Cryst.* B27, 846.
HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* 3, 210.
LEE, J. D. & BRYANT, M. W. R. (1969). *Acta Cryst.* B25, 2497.

Table 2. *Interatomic distances and angles with standard deviations in brackets for γ -Ca₂SiO₄*

(a) Distances	Multiplicity	
Ca(1) octahedron		
Ca(1)—O(1)	2	2.355 (6)
Ca(1)—O(2)	2	2.311 (6)
Ca(1)—O(3)	2	2.388 (8)
O(1)—O(2)	2	3.441 (2)
O(1)—O(2)	2	3.161 (10)
O(1)—O(3)	2	3.537 (7)
O(1)—O(3)	2	3.152 (11)
O(2)—O(3)	2	2.610 (8)
O(2)—O(3)	2	3.909 (9)
Ca(2) octahedron		
Ca(2)—O(1)	1	2.442 (8)
Ca(2)—O(2)	1	2.286 (8)
Ca(2)—O(3)	2	2.385 (6)
Ca(2)—O(3)	2	2.426 (6)
O(1)—O(3)	2	3.161 (10)
O(1)—O(3)	2	3.456 (7)
O(2)—O(3)	2	3.234 (8)
O(2)—O(3)	2	3.630 (8)
O(3)—O(3)	1	2.613 (8)
O(3)—O(3)	2	3.307 (7)
Si(1) tetrahedron		
Si(1)—O(1)	1	1.634 (9)
Si(1)—O(2)	1	1.655 (8)
Si(1)—O(3)	2	1.657 (6)

Table 1. *Atomic parameters and isotropic temperature factors with standard deviations in bracket for γ -Ca₂SiO₄*

	x	y	z	B (Å ³)
Ca(1)	0.0	0.0	0.0	0.44 (2)
Ca(2)	-0.0096 (5)	0.2809 (2)	0.25	0.38 (2)
Si(1)	0.4283 (6)	0.0959 (3)	0.25	0.23 (3)
O(1)	-0.2502 (16)	0.0926 (7)	0.25	0.55 (8)
O(2)	0.2981 (16)	-0.0393 (6)	0.25	0.49 (7)
O(3)	0.2954 (11)	0.1620 (4)	0.0567 (8)	0.38 (5)

Table 2 (cont.)

O(1)—O(2)	1	2.730 (11)
O(1)—O(3)	2	2.765 (9)
O(2)—O(3)	2	2.610 (8)
O(3)—O(3)	1	2.613 (8)
Average values		
Ca(1)—O		2.351
Ca(2)—O		2.386
Ca—O		2.369
Si—O		1.645

(b) Angles

Ca(1) octahedron		
O(1)—Ca(1)—O(2)	2	84.9 (2)
O(1)—Ca(1)—O(3)	2	95.0 (2)
O(1)—Ca(1)—O(3)	2	83.5 (2)
O(1)—Ca(1)—O(3)	2	96.5 (2)
O(2)—Ca(1)—O(3)	2	67.4 (2)
O(2)—Ca(1)—O(3)	2	112.5 (2)
Ca(2) octahedron		
O(1)—Ca(2)—O(3)	2	80.9 (2)
O(1)—Ca(2)—C(3)	2	91.4 (2)
O(2)—Ca(2)—O(3)	2	100.7 (2)
O(2)—Ca(2)—O(3)	2	87.6 (2)
O(3)—Ca(2)—O(3)	1	65.2 (2)
O(3)—Ca(2)—O(3)	2	86.8 (2)
O(3)—Ca(2)—O(3)	1	120.7 (2)

Table 2 (cont.)

Si(1) tetrahedron		
O(1)—Si(1)—O(2)	1	112.2 (4)
O(1)—Si(1)—O(3)	2	114.8 (3)
O(2)—Si(1)—O(3)	2	104.4 (3)
O(3)—Si(1)—O(3)	1	105.0 (3)

The results confirm the structure found by Smith, Majumdar & Ordway (1963), but show that the distortion of the SiO₄ tetrahedron found by these workers is not real.

The author wishes to thank Miss S. Melzer for her assistance. The work was supported by the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF). Calculations were done on an IBM 7094 computer at the Deutsches Rechenzentrum Darmstadt, Germany.

References

- CZAYA, R. (1970). *Z. anorg. allgem. Chem.* In the press.
 SMITH, D. K., MAJUMDAR, A. & ORDWAY, F. (1963). *Acta Cryst.* **18**, 787.
 YAMAGUCHI, G., ONO, Y., KAWAMURA, S. & SODA, Y. (1963). *J. Ceram. Assoc. Japan*, **71**, 9, 21.
 YANNAQUIS, N. (1955). *Rev. Matér. Constr.* **480**, 213.

Acta Cryst. (1971). B27, 849

Crystal data and structure of [(NH₃CH₂CH₂)₂NH₂]Cl(CuCl₄) at 20 °C and 120 °C. By GARY L. FERGUSON and B. ZASLOW, *Department of Chemistry, Arizona State University, Tempe, Arizona 85281, U.S.A.*

(Received 4 February 1970 and in revised form 19 August 1970)

Cell constants for [(NH₃CH₂CH₂)₂NH₂]Cl(CuCl₄) are $a = 7.117 \pm 0.004$, $b = 23.78 \pm 0.01$ and $c = 7.342 \pm 0.004$ Å at 20 °C; the space group is *Pnma*. Atomic parameters have been determined from zero and higher level precession data. The compound exhibits a network of planar CuCl₄²⁻ ions, and thermochromism is observed both above and below room temperature. X-ray data indicate that heavy atom positions at 120 °C are essentially unchanged from their values at 20 °C.

Although originally characterized as a CuCl₄²⁻ salt (Jonassen, Crumpler & O'Brien, 1945), it has been established that bis-(2-ammonioethyl)ammonium monochloride tetrachlorocuprate(II), [(NH₃CH₂CH₂)₂NH₂]Cl(CuCl₄), is a double salt having both Cl⁻ and CuCl₄²⁻ ions (Zaslow & Ferguson, 1967). Inasmuch as the CuCl₄²⁻ ion can demonstrate both a tetrahedral geometry (*e.g.* Morosin & Lingafelter, 1961) and a square-planar geometry (Willett, 1964), and high-temperature crystal data have not previously been recorded for thermochromic CuCl₄²⁻ salts, the following details of the structure of [(NH₃CH₂CH₂)₂NH₂]Cl(CuCl₄) are of interest.

The method of Jonassen, Crumpler & O'Brien (1945) was used to prepare [(NH₃CH₂CH₂)₂NH₂]Cl(CuCl₄). Crystals are yellow plates at room temperature, become pale green below room temperature, and convert to orange-brown upon heating to 120 °C. Specimens suitable for X-ray analysis were obtained by slow evaporation of water from an aqueous solution of the compound; their diffraction symmetry is orthorhombic, *mmm*. Cell constants were obtained from measurements of a Guinier powder diagram,

and are $a = 7.117 \pm 0.004$, $b = 23.78 \pm 0.01$ and $c = 7.342 \pm 0.004$ Å at 20 °C. Conditions for reflection are none for *hkl*, $k + l = 2n$ for *0kl*, and $h = 2n$ for *hk0*. Possible space groups are *Pnma* or *Pn2₁a*; subsequently, application of the *N(z)* test (Howells, Phillips & Rogers, 1950) fixed the space group as *Pnma*. The calculated density, assuming $Z = 4$, and the observed density determined by flotation in acetone and bromoform are 1.85 and 1.87 g.cm⁻³, respectively.

All intensity data were obtained from a crystal having dimensions 0.15 × 0.02 × 0.2 mm. Precession photographs taken with Zr-filtered Mo *K*α radiation at 20 °C yielded 286 independent data. Timed exposures were rated visually and intensities were obtained for the levels, *h0l*, *h2l*, *h3l*, *h4l*, *h6l* and *hk0*. Intensities were not evaluated from photographs of the levels *h1l* and *h5l*; only a small number of extremely weak reflections were detected at these levels, except for 210, 250, 450 and 650 which were processed with *hk0* data. Data reduction and other calculations utilized a modified version of the *X-ray 63* program (*Crystal Structure Calculations System, X-ray 63*, 1964). Absorption corrections were not applied and hydrogen atoms were neglected.