THE CRYSTALLOGRAPHY OF "COESITE"*

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ABSTRACT

The high pressure form of SiO_2 known as "coesite" or "silica C" is monoclinic, space group Cc or $C2/c$. However, it is dimensionally hexagonal, with $a_0=c_0$ and $\beta=120°$. Crystal measurements in general are very poor, but the x-ray data are excellent, and give the following results: $a_0=7.23$ Å, $b_0=12.52$ Å, $c_0=7.23$ Å; $d_{001}=d_{100}=d_{020}$. Two types of twinning are found, (100) and (021), chiefly based on x-ray results rather than morphology. All twin reflections either coincide with reflections of different hkl, or occupy forbidden positions. If untwinned as well as twinned crystals had not been available, it is doubtful if the space group assignment could have been made.

Through the courtesy of Dr. N. W. Thibault, Assistant Director of Research and Development, Norton Company, Worcester, Mass., the writer was provided with a sample of the new high pressure form of SiO_2 (Coes, 1953) which was named "coesite," but since it has not been found in nature, the alternative name "silica C" was also proposed (Sosman, 1954). This material was prepared in the Research Laboratories of the Norton Company. It is extremely interesting, not only as an additional polymorph of SiO_2, but also because of some unusual crystallographic features.

The material is colorless and transparent. A few individual crystals are found with simple forms which suggest gypsum crystals. Others are more complex, with no conspicuous zone development. Much of the material is in the form of aggregates of extremely small crystals less than 0.1 mm. in length. The maximum dimension found on the crystals used in this study was 0.6 mm., and most were less than 0.4 mm. Great difficulty was encountered in mounting the crystals, and many were lost at various stages of measuring and x-raying. Those resembling gypsum were easily oriented, but for the others the orientation could in many cases be determined, if at all, only after measuring the angles.

The usual procedure was to sketch the crystals in various positions under high power binoculars. Because of the transparency, it was difficult to see the outline of an individual face unless it was oriented so as to reflect light. After mounting under a binocular microscope, the crystal was transferred to an optical goniometer and an attempt made to correlate the measured angles with the sketches. If successful, the crystal was then transferred to the x-ray goniometer. Although the crystals appear brilliant, there is some rounding of the faces, and the optical goniometer measurements were usually of poor quality. It is very doubtful if such measurements alone would have been sufficient to determine the sym-

metry or the twin laws. Some faces could not be identified with certainty. Every crystal examined showed (010), usually as the largest form, and at least some faces of the prism (130). Additional faces were very variable and rarely were symmetrically arranged.

Fortunately, the x-ray data were much superior to the optical measurements. Excellent Weissenberg and precession photographs were obtained. These give accurate cell dimensions and the space group, and in addition reveal in some cases twinning on 100 which was not even suspected from the optical goniometric measurements. The x-ray films also show that reentrant angles observed on some crystals are caused by twinning on (021).

The x-ray data verify the monoclinic character suggested by the gypsum-like crystals, but also show that while monoclinic in symmetry, the crystals are dimensionally hexagonal, that is, $a = c$; $\beta = 120°$. In addition $d_{001} = d_{020}$, so that the 021 twin plane is exactly at 45° with respect to b^* and c^*, and brings them into exact coincidence on the x-ray films. The extinctions hkl with $h+k$ odd indicate an end-centered lattice, and the absence of $h0l$ reflections with l odd show that the 010 plane is a c glide plane. There is no x-ray evidence to distinguish between the two space groups Cc and $C2/c$, and the morphological data are too poor to allow a choice to be made.

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X-RAY DATA
Cu K$\alpha = 1.5418$ Å

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	Extinctions
$a_0 = 7.23$ Å	hkl missing with $h+k$ odd hence C lattice.
$b_0 = 12.52$ Å	
$c_0 = 7.23$ Å	
$\beta = 120°$	$h0l$ missing with l odd hence 010 is a c glide plane.
$d_{100} = d_{001} = d_{020}$	Twinning on (100) and (021) revealed by Weissenberg
Cell volume 536 Å^3	photographs.

Goniometric measurements on six crystals gave the data in the following table. The quality of most of the signals was very poor. The calculated values are based on the unit cell dimensions.

Many of the crystals are flattened parallel to (010), and most of these have a common direction of elongation, which is chosen as the c axis. Since with an angle β of 120°, pairs of faces such as (001) and ($\bar{1}$01), or (011) and ($\bar{1}$11), have the same rho angles, they cannot be distinguished morphologically, and consequently there is a dual choice for the a axis, each with the same value of β. However, x-rays easily make a distinction.

COESITE. MONOCLINIC; m OR $2/m$
$a:b:c = 0.577:1:0.577$; $\beta = 120°$. $p_0:q_0:r_0 = 1.0:0.5:1$
$p_0' = 1.1547$, $q_0' = 0.5773$, $x_0' = 0.5773$

	Form	No. times obs.	Observed range		Calculated	
			ϕ	ρ	ϕ	ρ
c	001	2	89°50′–90°30′	29°45′–30°14′	90°00′	30°00′
b	010	all xls.	0 00	90 00	0 00	90 00
i	130	all xls.	33 41 –34 10	89 52 90 10	33 42	90 00
m	110	2	62 05 –64 03	89 35 90 30	63 26	90 00
w	011	3	44 49 –46 35	38 45 –39 48	45 00	39 15
v	021	2	@ 25°	@ 52°	26 34	52 14
D	$\bar{1}01$	2	−89 34 –90 29	29 46 –30 15	−90 00	30 00
r	111	2	71 26 –71 45	61 20	71 34	61 18
R	$\bar{1}11$	5	−44 49 –46 20	38 45 –39 50	−45 00	39 15

One choice gives an end-centered lattice, the other a body-centered lattice. The former has been used for the description of coesite.

There is no significant deviation from the value of 120° for β on either the Weissenberg or precession photographs, nor is there any detectable difference in the values for a_0 and c_0. The 120° angle and the dimensional equality of a and c means that there is a third direction bisecting the angle between a and c which is likewise equal. Thus the zero level Weissenberg, with rotation about the b axis, shows three central lattice lines 60° apart, all with the same spacings. However, both missing reflections and variations in intensities definitely reveal the absence of a six fold axis of symmetry. The true monoclinic character is most clearly revealed in the upper level photographs, which have only a two fold axis of symmetry. The upper levels also definitely locate the c^* direction, and hence the a axis. Figure 1 shows the reciprocal lattice for the 0, 1 and 2 levels for this orientation.
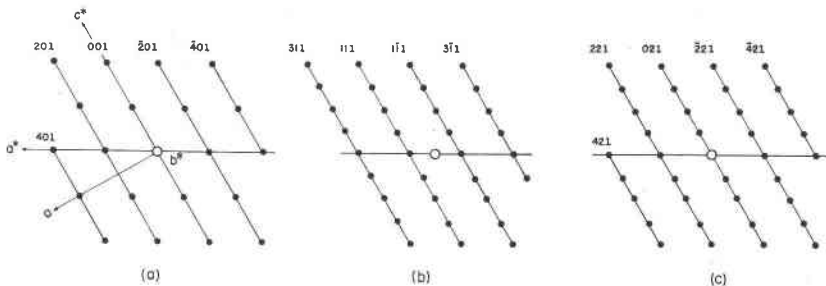

FIG. 1. Reciprocal lattice levels with rotation about the b axis. (a) 0-level, pseudohexagonal symmetry. (b) and (c) 1-level and 2-level, with symmetry C_{2l}.

MORPHOLOGY

More than a dozen crystals were observed which showed some resemblance to gypsum crystals. Crystals of this kind were referred to in the original description as "hexagonal plates with unsymmetrical extinction." Some of the various combinations of terminal faces are shown in Fig. 2 *a*, *b*, *c*, *d*. Other crystals were flattened on (010) and showed at
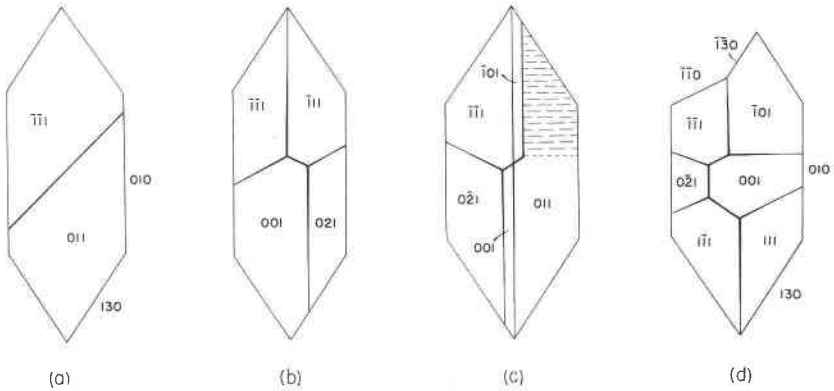

FIG. 2. Variable terminations on crystals. (*a*), (*b*), and (*c*) untwinned. (*d*) twinned on 021, as shown by *x*-ray data.

least some of the faces of the (130) prism, but with no terminal faces. The majority of the single crystals, although showing one or more well-developed faces, presented no obvious clue as to their orientation or the identity of the faces.

TWINNING

Twining on (100) in gypsum gives the familiar "swallow tail" effect. The coesite crystals twinned on (100) showed no such re-entrant angle. The developed end of the twins usually showed a more complex development than did untwinned crystals. But since in the latter the faces (001) (011) and (0$\bar{1}$1) are symmetrical in position with ($\bar{1}$01), ($\bar{1}$11) and ($\bar{1}\bar{1}$1), respectively, there is no morphological evidence that twinning is present. All faces on a twinned crystal can be indexed as if it were a single crystal.

Excellent Weissenberg photographs of both twinned and untwinned crystals, with rotation about the *c* axis, were obtained. If only twinned crystals had been available, a very puzzling situation would have resulted. There is no doubling of spots, as is common with twinned crystals. Since every plane in one twin portion is exactly parallel to a different plane in the other, all reflections can be indexed as from a single crystal. The zero level photographs give no evidence of twinning, for the 0-level

symmetry is C_{2l} with $hk0$ symmetrical to $h\bar{k}0$ across 010, and $hk0$ symmetrical to $\bar{h}k0$ across 100 (Fig. 3b). The first level films, however, are quite distinctive; $hk1 = h\bar{k}1$ across 010, but $hk1 \neq \bar{h}k1$ across 100. The monoclinic shift between the 0-level and the 1-level is exactly one half of the a^* spacing (Fig. 3a). The 1-level reciprocal lattice of an untwinned crystal is shown in Fig. 3c. There is a single plane of symmetry perpendicular to the b axis. Both $hk1$ with $h+k$ odd and $h01$ are missing, because of the C lattice and the c glide. On twinned crystals, every permissible reflection is repeated across the b-c plane and falls exactly on a
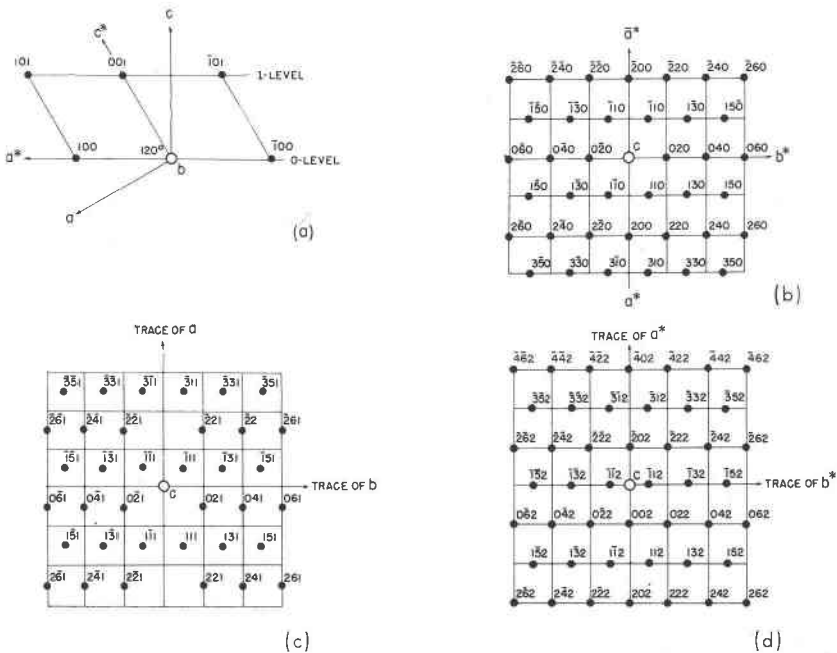
FIG. 3. (a) Monoclinic shift for 1-level reciprocal lattice is exactly $1/2\ a_0^*$ spacing. (b), (c) and (d) 0–1–2-levels of reciprocal lattice with rotation about the c axis.

lattice position, but in every case it is a forbidden position, with $h+k$ odd. This is perfectly obvious when untwinned crystals are also found, but if only twinned crystals were available, the situation could easily be misinterpreted.

The second level photograph resembles that of the zero-level, with apparent C_{2l} symmetry, resulting from the doubled monoclinic shift (Fig. 3d). Every possible reflection with a given value of h has a twinned reflection in a legitimate position, corresponding to $-(h+z)$. Thus 002 is symmetrical to $\bar{2}02$, 112 to $\bar{3}12$, etc. This is not merely an approximate

coincidence. In no case have doubled spots been observed. The chief difference between the second levels of twinned and untwinned crystals is that the latter have occasional random absences which may not be found on twinned crystals, and some intensities are different, because most reflections are composite ones.

Two crystals with 021 twinning were found. The first one to be encountered is shown in Fig. 2d. The re-entrant angle is conspicuous, but its relation to the twinning is unknown. In the figure the faces are all indexed as belonging to one individual, for here likewise there is exact
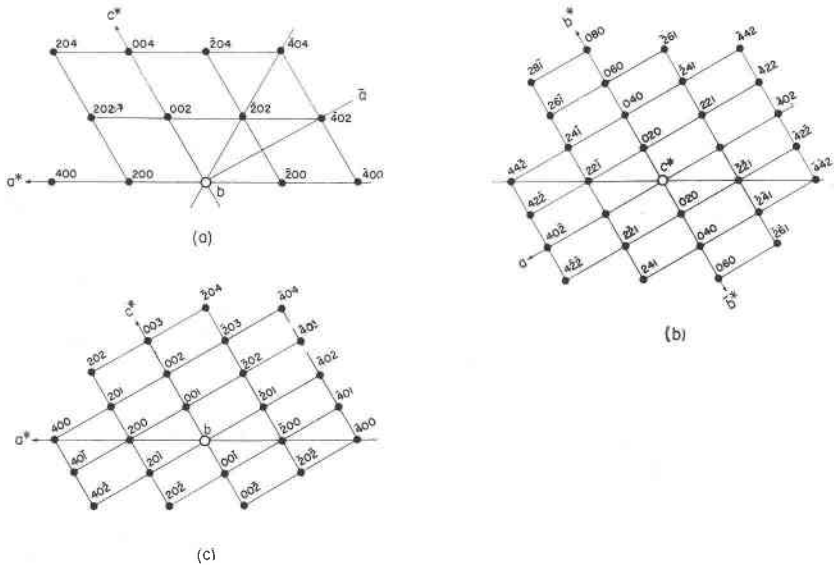
FIG. 4. Reciprocal lattice for 0-level, b axis rotation. (a) untwinned crystal. (b) crystal twinned on 021, indexed for rotation about c^*. (c) same as (b), but indexed for b axis rotation, showing forbidden reflections $h0l$ with l odd.

parallelism between different planes in the two parts, and there is no certain way of telling which is which. The presence of 021 twinning was deduced solely from the x-ray data.

The effect of 021 twinning is to bring the $b^* - a$ plane into exact coincidence with the $c^* - a$ plane. Every plane hkl in one portion is parallel with an HKL plane in the other, the transformation being: $H = h$, $K = h + 2l$, $L = (-h + k)/2$. Here again the occurrence of both twinned and untwinned crystals made an interpretation possible. For a 0-level, c axis rotation, the Weissenberg photograph of an untwinned crystal has certain random absences which are not apparent for the twinned crystal,

because these positions may also correspond to reflections from the other portion. Various intensity differences are also noted, because many of the reflections from the twin crystal may be dual.

The most striking evidence of the 021 twinning is found in the 0-level, b axis rotation films. The Weissenberg photograph of an untwinned crystal shows three central lattice lines 60° apart, which are 001 (c^*), $h00$ (a^*) and $h0\bar{h}$. The corresponding Weissenberg of a twinned crystal shows superimposed on this the equivalent of a rotation about the c^* direction, with its b^* central lattice line coinciding with c^* from the other. This relationship is shown in the reciprocal lattice diagrams in Fig. 4. It will be noticed that the twinned crystal gives a larger number of reflections than the untwinned crystal. If they are all indexed as $h0l$ reflections (i.e. b axis rotation) half of the reflections do not agree with the extinctions for the c glide — $h0l$ absent for l odd as shown in Fig. 4c.

Later another crystal was found which did show morphological evidence of 021 twinning. This had a 90° re-entrant angle. Since the 021 plane is at 45° to both b^* and c^*, (010) in one part should be perpendicular to (010) in the other. The common edge of the re-entrant angle is parallel to the a axis. A zero level Weissenberg taken about this common a axis should give a composite photograph, with b^* and c^* (90° apart) from one part coinciding with c^* and b^* of the other. This proved to be the case. There is no doubling of spots, for reflections from both parts coincide. The photograph appears like that of a tetragonal crystal, with symmetry C_{4l}, which is quite different from the zero level, a axis rotation, of an untwinned crystal, where the symmetry is C_{2l}.

This crystal has numerous tiny faces, and other minor re-entrant angles, but many of the reflections were poor, and only five faces could be identified, in addition to the two 010 faces 90° apart. In contrast to the poor morphological data, the Weissenberg photographs were excellent.

One interesting consequence of the 90° re-entrant angle is that when rotated about the a axis on the vertical circle of the goniometer, not only did the reflections from the two 010 planes occur 90° apart, but a continuous weaker signal persisted during the interval between. This is a modification of the well known phenomenon that a beam of light in a plane normal to two mirrors at 90° to each other will be reflected back parallel to itself at any angle of incidence.

UNIT CELL CONTENTS

One puzzling situation occurs with respect to the value obtained for the unit cell contents. Using the cell dimensions as determined from Weissenberg photographs, and a density of 3.01 as determined by the

Norton Company and checked by the writer, the number of formula weights in the unit cell is about 17. Because of the pseudohexagonal character of the monoclinic cell, a value of 18 had been anticipated. However, the space groups Cc and $C2/c$ provide equivalent positions of 4 and 8, respectively, which would require a value of 16.

This discrepancy seems to be too large to be attributed to errors in determining either cell dimensions or density. Chemical tests at the Norton Company included complete volatilization on heating with ammonium bifluoride, and transformation, without change in weight, into silica glass and cristobalite when heated in platinum at 1700° C. These would indicate the new substance is a compound of nothing but silicon and oxygen. A quantitative chemical analysis would be very desirable, to find out if there is any deviation from a strict stoichiometric composition.

REFERENCES

(1) COES, L., JR. (1953), A new dense crystalline silica: *Science*, **118**, 131–132.
(2) SOSMAN, R. B., (1954), New high-pressure phases of silica: *Science*, **119**, 738–739.