

The reviewer has used the first volume of the English translation, together with the second volume of the German edition, in a course for beginning graduate students, and has found it very satisfactory, especially when supplemented with problems and special readings. It is much to be desired that the translation of the second volume be not delayed.

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SPECIAL ARTICLES

THE STRUCTURE OF HIGH- (OR β -) QUARTZ¹

At temperatures below 575° C. crystals of quartz have the symmetry of the enantiomorphic hemihedral class of the rhombohedral division of the hexagonal system (point group 3D). An inversion takes place at this temperature, however, and above 575° C. the symmetry is increased to that of one of the truly hexagonal crystal classes. When α - (or low) changes to β -quartz a single crystal of the former becomes transformed into a single and similarly oriented crystal of the latter. This fact permits the investigation of the X-ray diffraction effects from single crystals as well as from crystalline aggregates of β -quartz.

Powder, Laue and spectrum photographs have been made from β -quartz in the course of a series of X-ray diffraction studies of crystals at elevated temperatures. The data from these photographs have been found to be sufficient to yield a unique solution to the problem of the atomic arrangement in this form of silica.

A print has been published of a Laue photograph² of quartz above its inversion point. Spectrometer measurements³ from several simple planes have also been recorded. No structure, however, has been deduced from either of these earlier sets of observations.

Crystallographic measurements have shown β -quartz to have an axial ratio very close to that of α -quartz— $c_\beta=1.0926^4$ as opposed to $c_\alpha=1.0999$. The hexagonal unit cell of α -quartz which agrees with all attainable diffraction data has dimensions $a_0=4.903\text{\AA}^5$, $c_0=5.39_3\text{\AA}^6$ and contains three molecules of SiO_2 .

¹ A paper (*J. Soc. Glass Technology*, Sept., 1925) has just appeared in which W. H. Bragg describes a structure for β -quartz. His atomic arrangement seems to be essentially identical with the one deduced here.

² F. Rinne, "Die Kristalle als Vorbilder des feinbaulichen Wesens der Materie" (Berlin, 1921), p. 35.

³ R. E. Gibbs, *Proc. Roy. Soc. A*, 107, 561 (1925).

⁴ R. Grossmann quoted in F. Rinne, *op. cit.*, p. 89.

⁵ M. Siegbahn and V. Dolejšek, *Zeit. f. Physik*, 10, 159 (1922).

The only simple unit cell for β -quartz that can account for the data from powder photographs and from six Laue photographs is a similar one with $a_0=5.01\text{\AA}^7$, $c_0=5.47\text{\AA}^8$. Since the density⁶ of β -quartz is known to be $\rho(585^\circ)=2.518$, its unit cell likewise must contain three molecules of SiO_2 .

The hexagonal, rather than trigonal, symmetry of β -quartz is immediately apparent from the Laue photographs taken with the X-rays normal to the base (00-1). Since quartz above its inversion still shows rotary polarization, its class of symmetry must be either 6C or 6D. Crystallographic observations⁷ have been supposed to point quite conclusively to the latter. If this selection of crystal class is assumed to be correct, the following deduction leads uniquely to a structure for β -quartz which is in satisfactory accord with experiment.

The X-ray diffraction effects arising from atomic arrangements built upon the space groups isomorphous with 6D differ in the nature of the reflections observed from the plane (00-1). The present powder and spectrum photographs from β -quartz agree with the previous spectrometer measurements in showing only 3rd, 6th, etc., orders from this face. Its corresponding space groups⁸ consequently prove to be the enantiomorphic pair 6D-4 and 6D-5. There are numerous ways of arranging three silicon and six oxygen atoms according to the demands of these groups. All those structures which put oxygen atoms in special positions⁹ (a)-(f) are excluded by the presence of first-order Laue reflections from planes (2m, 2n.p), where m, n, and q are any integers and $p \neq 3q$. The eight remaining structures are obtained by combining (a) and (e), as silicon positions, with (g), (h), (i) or (j), as oxygen positions. Four of these, (a)(g), (a)(i), (e)(g), and (e)(i) place the oxygen and silicon atoms in the same planes parallel to (00-1). If, then, one of these groupings were the correct structure, the observed 3rd, 6th, etc., orders from the base should show a "normal decline" of intensity with order. Both the spectrometer observations¹⁰ and spectrum photographs indicate that

⁶ A. L. Day, R. B. Sosman, and J. C. Hostetter, *Am. J. Sci.*, 37, 1 (1914).

⁷ O. Mügge, *Neues Jahrb. f. Min.*, u.s.w. Festband, 1907, p. 181.

⁸ P. Niggli, "Geometrische Kristallographie des Discontinuuums" (Leipzig, 1919), p. 493; W. T. Astbury and K. Yardley, *Trans. Roy. Soc. (London)*, 224A, 221 (1924).

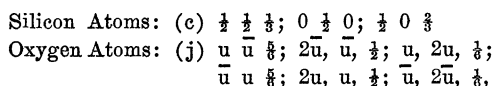
⁹ These designations of atomic positions are the ones used in R. W. G. Wyckoff, "An analytical expression of the results of the theory of space groups" (Washington, 1922), p. 165.

¹⁰ R. E. Gibbs, *op. cit.*

00.1(3) is not stronger than 00.1(6). These four arrangements may thus be excluded from further consideration.

Each of the four remaining possibilities (a)(h), (a)(j), (c)(h), and (c)(j) has only one variable parameter. It is consequently entirely feasible to calculate the nature of the diffraction effects to be expected from them for different values of the variable parameter u . A comparison of the results of such calculations with the principal aspects of the powder photographs and with the important intensity anomalies observed in the Laue photographs from β -quartz serves to eliminate all these structures except (c)(j). If in grouping (c)(j) the parameter u is chosen close to 0.20, then excellent agreement is found between calculated and observed intensities.¹¹

It can hence be concluded that the structure of β -quartz is that of the two enantiomorphic arrangements 6D-4, (c)(j) and 6D-5, (c)(j). The co-ordinate positions of the atoms in the hexagonal unit of 6D-4, for instance, are



where u has a value in the neighborhood of 0.20.

This structure agrees with the one deduced for β -cristobalite¹² in placing a tetrahedron of oxygen atoms about each silicon atom. In cristobalite this tetrahedron was necessarily regular; symmetry does not require such a regularity in quartz, but the value found for u is such as to bring about at least an approach to this condition. From data now being obtained through the analysis of prism face Laue photographs it is hoped to be able to limit the oxygen parameter more narrowly, and thus to gain a more quantitative measure of this approach to regularity. No molecules of SiO_2 could be distinguished in crystals of β -cristobalite; neither does this structure for β -quartz show clear evidence for SiO_2 or $(\text{SiO}_2)_x$ molecules.

Though their Laue photographs exhibit very different intensities of reflections, the powder photographs of α - and of β -quartz are astonishingly similar. This is precisely what would be expected if the change from one form of quartz to the other involves only a relatively slight atomic rearrangement. The numer-

¹¹ Arrangements (a)(h) and (a)(j) would not have been expected because they make the three silicon atoms all lie on a single axis and thus place them closer together than previous experience has indicated as probable; similarly (c)(h) is unlikely because it associates oxygen atoms more intimately with one another than with silicon atoms.

¹² R. W. G. Wyckoff, *Am. J. Sci.*, 9, 448 (1925).

ous other known facts about quartz agree with this supposition.

A more detailed description of this structure, together with a statement of the extent to which it agrees with experiment, will be published in the *American Journal of Science*. This experimental evidence and a tabulation of the distinguishing criteria for all special cases of the hexagonal space groups will appear in the *Zeitschrift für Kristallographie*.

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A NEW METHOD FOR THE STUDY OF SOFT X-RAYS¹

A new method for determining ionization and resonance potentials is found and applied in determining such critical limits of the elements composing photographic emulsions. At this writing the soft X-ray region between 100 and 750 volts has been studied.

A beam of electrons, having velocities uniformly distributed over the range under investigation, is spread into a band by means of a magnetic field. The velocity possessed by the electrons in any given part of this band is determined from the geometry of the apparatus and the strength of the magnetic

TABLE I

Volts ± 2	$\sqrt{V/R}$	Interpretation
135	10	
173	12.8	Br; $4_1 \rightarrow 3_2$
184	13.5	Br; $4_1 \rightarrow 3_2$
193	14.25	Br; M_{III}
202	14.9	Br; M_{II}
255	18.8	C; $K\alpha$
265	19.6	Br; M_I
273	20.15	
282	20.8	
288	21.25	C; K absorption
306	22.6	K; L absorption
323	23.9	Ag; $4_2 \rightarrow 3_3$
333	24.6	Ag; $4_2 \rightarrow 3_3$
345	25.5	
350	25.85	
376	27.8	Ag; M_V , or N; $K\alpha$
384	28.4	Ag; M_{IV}
404	29.8	N; K absorption
440	32.5	
497	36.7	O; $K\alpha$
548	40.45	O; K absorption
562	41.5	Ag; $4_3 \rightarrow 3_2$
572	42.2	Ag; M_{III}
597	44.1	Ag; M_{II}
664	49.0	Ag; $4_2 \rightarrow 3_1$
695	51.2	
730	53.9	Ag; M_I
762	56.3	

¹ Preliminary report.