

An X-ray study of the temperature dependence of the quartz structure

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Abstract : The structure analysis of a natural transparent quartz crystal was carried out using X-ray diffraction amplitudes at temperatures ranging from 298 K to 1126 K. The temperature dependence of the atomic probability density function (PDF), the mean-square displacement (MSD) and the orientation of thermal-motion ellipsoids was analysed in detail and shown to be useful for discussing the β -quartz structure.

There is no obvious X-ray diffraction evidence supporting a disordered model for β -quartz as previously suggested by neutron diffraction work. Instead, a more weakly disordered or even ordered model seems to be in better agreement with the observations. The characteristic feature of our model is that oxygen atoms practically undergo librational motion around the Si-Si lines, being correlated with silicon atoms oscillating along the two-fold axes in $\langle 100 \rangle$. In this model, the motion of SiO_4 tetrahedra is not rigid, but is associated with considerable bending of the O-Si-O angles. By contrast, the Si-O-Si bonding planes are kept rigid. At 848 K, the Si-O bond length is 1.62 Å and the Si-O-Si angle is 145°, whereas the O-Si-O angles range from 100 to 118°.

The MSDs for oxygen and silicon atoms in the directions closely related to the displacement vectors of the α - β transition show an anomalous temperature dependence ; with increasing temperature, there is a decrease of MSD immediately after the transition, and then a gradual change to increasing values at around 950 K.

Key-words : quartz structure, thermal vibrations, temperature dependence, phase transition, probability density function, X-ray diffraction.

Introduction

The α - β phase transition of quartz is well known to occur at about $T_0 = 846$ K, and there have been a large number of studies on the structure and physical properties of the two phases. Only a few of these works involve high-temperature structure refinements based on diffraction data (Young, 1962 ; Wright and Lehmann, 1981) or inelastic neutron scattering data (Boysen *et al.*, 1980).

Two main models have been proposed for the β -quartz structure, which can be briefly summarized as follows :

(1) The structure is hexagonal and has silicon atoms at positions with site symmetry 222 and oxygen atoms on $\langle 210 \rangle$ with site symmetry 2. These sites correspond to the midpoints

between the two sets of α_1 and α_2 positions in α -quartz related by Dauphiné twinning.

(2) The structure is hexagonal as a result of atom disorder over the α_1 and α_2 orientations.

Although Young (1962) preferred the first model in his X-ray diffraction study, most authors after him interpreted their data on the basis of the second model, with some modifications (*e.g.* Tendeloo *et al.*, 1976 ; Wright and Lehmann, 1981 ; Boysen *et al.*, 1980 ; Liebau and Böhm, 1982). Tendeloo *et al.* observed with the electron microscope that twin domains were formed just below the transition temperature and became finer as the transition approached. Furthermore, the domain walls appeared to be constantly vibrating, so that a given region belonging to an α_1 domain might become an α_2 , and *vice versa*. Accordingly,

these authors have suggested that the β -quartz structure is a time average of α_1 and α_2 orientations. Liebau and Böhm (1982) have proposed that, just below the transition temperature, chains of *quasi-rigid* tetrahedra begin to fluctuate between the α_1 and α_2 orientations with long-range correlation, thus yielding microdomains. Instead, above the transition temperature, the long-range correlation ceases, and each chain fluctuates independently between the two minima in a double-minimum potential.

Wright and Lehmann (1981) examined a split-atom model in a least squares refinement of neutron diffraction data at 863 K, and concluded that oxygen atoms were disordered over the α_1 and α_2 positions. However, their conclusion was based on the fact that the least-squares refinement using a split-atom model resulted in a substantially lower R-value compared with the first model. This might simply mean that the atomic probability density function (PDF) is spread out sufficiently around its maximum to be better approximated by the split-atom model. Such a PDF contour map might also be derived from the first model with elongated potential troughs. In the author's view, it is very difficult to answer the problem by using diffraction data obtained at a single temperature.

The recent discovery of an intermediate phase (IP), which appears in a narrow temperature range of about 2° between α and β (Gouhara *et al.*, 1983; Dolino *et al.*, 1983), shows that there still remain some problems about structural changes in quartz. In addition, the previous structural studies have been carried out using up to second-order terms in the structure-factor expression, in spite of various reported indications of an anharmonic character in quartz. Especially for higher temperatures, the inclusion of higher-order terms might result in more accurate estimation of the atomic PDFs. In this study, higher order terms were introduced into the structure factor expression, and a split-atom model has also been considered to characterize the β - and α -quartz structures more accurately.

Experimental procedure

Several fragments were cut from a clear prismatic crystal of natural quartz and were ground

into apparently perfect spherical shape by the Bond method (Arndt and Willis, 1966). X-ray diffraction data were obtained using graphite-monochromated MoK_α radiation on a Philips 4-circle diffractometer. Intensities and cell dimensions were measured for one of these specimens at 18 different values of temperature, ranging from 298 K to 1126 K (8 points for α -quartz and 10 for β). The grain size of the specimen varied over a range from 0.220 to 0.230 mm. The specimen was heated by an electric resistance heater with a PID controller. Temperatures were calibrated by the melting points of pure Sn (504.9 K) and Zn (692.6 K), and were controlled to within 1 K. The two set-points and room temperature were well fitted to a straight line, from which the α - β transition temperature of 845 K could be derived, in good agreement with the other observations. This line also yielded the melting points of Sn, Zn and Al (933.4 K) as 505, 697 and 930 K, respectively. In this study, no effort was made to determine the two-step transition β -IP- α .

Three sets of symmetry-related reflections were measured in the range of Bragg angles from 3 to 40° , using the ω -scan if $\theta < 20^\circ$, and the $\omega/2\theta$ scan at higher θ values, with scan width given by $2^\circ + 0.3 \tan\theta$. The detector aperture was 2° for the horizontal and 1.5° for the vertical direction. The reflections were omitted if $I_{\text{top}} - 2 I_{\text{top}}^{1/2} < I_{\text{bck}}$, where I_{top} is peak intensity and I_{bck} is background. In total, about 470 reflections for β (space group $P6_222$) and 900 for α ($P3_221$) were measured at each temperature. During measurement of integrated intensities, temperature was controlled within 1° at best and 6° at worst. Reflections were corrected for Lp factors, absorption ($\mu R \approx 0.105$) and 1-phonon thermal diffuse scattering (TDS). The TDS contribution was estimated using the computer program SXTDS1 (Kurittu and Merisalo, 1977), based on Merisalo and Kurittu (1978), and the elastic constants from several authors (Atanasoff and Hart, 1941; Atanasoff and Kammer, 1941; Kammer *et al.*, 1948; Smagin and Mil'shtein, 1975). According to these calculations, the maximum of TDS contribution reached 25 % of the intensity for some reflections at 1126 K. The disagreement between symmetry-related reflections ranges from 1.9 to 3.0 %.

The integrated intensities of some strong reflections, including 011 and 101, were measured at different azimuthal angles in order to

examine possible anisotropy around the diffraction vectors. Assuming a correct alignment of the crystal, a large difference in intensity, if it existed, would suggest the possibility of anisotropic extinction for the spherical crystal. The maximum intensity-difference was about 5 %, even for the strongest 011 reflection at room temperature. From this and the small disagreement between symmetry-related reflections, it was decided to attempt extinction corrections first with isotropic models in the following refinement.

Line profiles of 36 reflections were measured at each temperature and used in least-squares calculations to determine the cell constants: these are listed in Table 1 and plotted against temperature in Fig. 1. The room temperature values, $a = 4.9137(8)$ and $c = 5.4047(12)$ Å, are in good agreement with the literature: $a = 4.9132$ – 4.9139 and $c = 5.4049$ – 5.4052 Å reported for synthetic samples and $a = 4.9134$ and $c = 5.4050$ Å for colourless natural quartz (Cohen and Sumner, 1958).

Refinement

Refinement was carried out using the least-squares program LSGC (Kihara *et al.*, 1986),

Table 1. Cell dimensions and volumes of natural quartz at different temperatures.

Temperature	a (Å)	c (Å)	v (Å ³)
298 (K)	4.9137(8)	5.4047(12)	113.01(5)
398	4.9209(4)	5.4091(5)	113.43(2)
498	4.9297(7)	5.4151(10)	113.97(4)
597	4.9384(7)	5.4213(10)	114.50(4)
697	4.9509(8)	5.4285(11)	115.23(5)
773	4.9628(9)	5.4360(13)	115.95(5)
813	4.9728(9)	5.4425(12)	116.56(5)
838	4.9841(12)	5.4500(17)	117.25(7)
848	4.9965(5)	5.4570(7)	117.98(3)
854	4.9968(5)	5.4576(8)	118.01(3)
859	4.9973(9)	5.4572(14)	118.03(5)
869	4.9971(6)	5.4574(9)	118.02(4)
891	4.9972(7)	5.4569(11)	118.01(4)
920	4.9972(7)	5.4571(11)	118.02(4)
972	4.9977(11)	5.4564(15)	118.03(6)
1012	4.9964(5)	5.4543(7)	117.92(3)
1078	4.9965(4)	5.4546(4)	117.93(2)

Esd's are given in parentheses.

which was derived from ORXFLS4 (the 1977 version of ORFLS by Busing *et al.*, 1962) in order to estimate coefficients from the first- to the sixth-order (x , b , c , d , e , g) in the Gram-Charlier expansion (Johnson and Levy, 1974). The structure factor $F(\mathbf{h})$ of a reciprocal lattice node $\mathbf{h}$ was calculated using the following

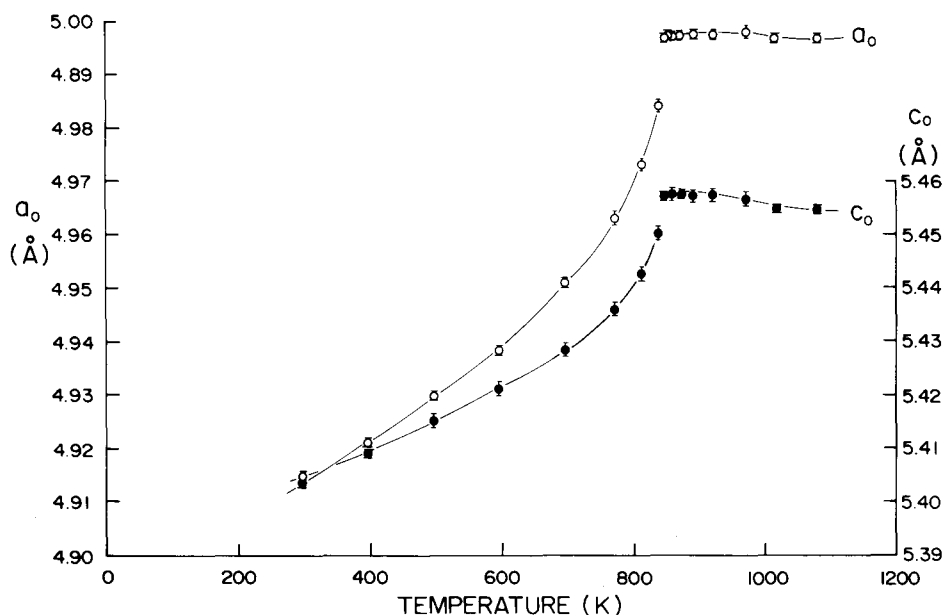


Fig. 1. Cell dimensions, a_0 and c_0 , of a natural transparent quartz crystal at different temperatures.

expression (in the repeated summation convention) :

$$F(\mathbf{h}) = \sum f_r \exp(-\beta_r) \exp(i\alpha_r) (1 - i\gamma_r + \delta_r + i\varepsilon_r - \zeta_r),$$

where f_r is the atomic scattering factor for atom r and h_{i-n} are the indices of $\mathbf{h}$,

$$\alpha_r = 2\pi x_r^i h_i,$$

$$\beta_r = b_r^{ij} h_i h_j,$$

$$\gamma_r = 4/3 \pi^3 c_r^{ijk} h_i h_j h_k,$$

$$\delta_r = 2/3 \pi^4 d_r^{ijkl} h_i h_j h_k h_l,$$

$$\varepsilon_r = 4/15 \pi^5 e_r^{ijklm} h_i h_j h_k h_l h_m,$$

$$\zeta_r = 4/45 \pi^6 g_r^{ijklmn} h_i h_j h_k h_l h_m h_n.$$

The terms after the second-order are called *higher-order* in this paper. The quantity minimized was $\sum w (|F_o| - k |F_c|)^2$ with $w = 1/\sigma^2$ (counting statistics), where k was a scale factor. Spherical atomic scattering factors were obtained from the table of Cromer and Waber (1974).

The agreement among the three data sets of symmetry-related structure amplitude was sufficiently good to justify taking averages of the observed $F(\mathbf{h})$. Refinement was carried out using such structure amplitude data for both α and β -quartz. Type I and II isotropic extinction models were tested, but only type I was successful, with slightly lower R values for a Lorentzian mosaic distribution (Becker and Coppens, 1974). Data relevant to this refinement are shown in Table 2.

α -quartz

The structure of α -quartz is known to have an ordered atomic arrangement, where silicon atoms are in position with site symmetry 2 along $\langle 100 \rangle$, and oxygen atoms in general position (Fig. 2). The refinement was first carried out with a conventional structure factor expression (represented as 2G), where the higher-order terms are omitted, and then with a more generalized expression including higher-order coefficients up to the fourth-order (4G).

The 2G refinement has 14 variables for the atomic parameters, but a total of 16 variables were refined, including a scale factor and an extinction factor. In the 4G refinement, 38 independent coefficients could be assigned for the third- and fourth-order terms, but some of them converged to magnitudes smaller than the corresponding esd's; these were assumed to be zero in the final stage of the refinements. The degree of parameter correlation is not serious.

Most structural studies of α -quartz (e.g. Zachariasen and Plettinger, 1965), have suggested that it is difficult to find quartz crystals entirely free of Dauphiné twinning. The measured intensities were accordingly tested for such twinning, using the following relations :

$$I_{hkl} = I'_{hkl} + a (I'_{hkl} - I'_{khl})$$

$$I_{khl} = I'_{khl} - a (I'_{hkl} - I'_{khl}),$$

Table 2. Structure refinement data for quartz.

α -quartz								
	298K*	398K	498K	597K	697K	773K	813K	838K
Nr	267	250	267	271	266	265	259	251
second-order refinements								
P	16	16	16	16	16	16	16	16
R	.017	.017	.016	.019	.020	.026	.029	.030
Rw	.027	.025	.023	.024	.030	.037	.014	.016
S	1.04	1.01	0.83	0.90	0.97	1.15	1.10	1.12
fourth-order refinements								
P	33	34	31	42	41	42	42	42
R	.017	.014	.018	.017	.021	.019	.019	.019
Rw	.022	.020	.021	.023	.027	.010	.009	.009
S	0.95	0.76	0.81	0.81	0.91	0.79	0.69	0.69

β -quartz										
	848K	854K#	859K	869K	891K	920K	972K#	1012K#	1078K	1126K#
Nr	152	144	144	139	153	140	141	135	139	115
second-order refinements										
P	10	10	10	10	10	10	10	10	10	10
R	.033	.030	.031	.033	.034	.030	.039	.038	.038	.035
Rw	.045	.044	.043	.045	.044	.043	.045	.046	.043	.038
S	1.39	1.39	1.36	1.48	1.35	1.36	1.40	1.38	1.32	1.17
fourth-order refinements										
P	23		23	22	23	22				23
R	.024		.021	.021	.024	.020				.028
Rw	.031		.028	.028	.029	.028				.031
S	1.01		0.96	0.97	0.95	0.91				1.00

Nr : number of reflections used, P : number of variables, R : $\sum |F_o| - |F_c| / \sum |F_o|$, S : $\{\sum w(F_o - F_c)^2\} / (Nr - P)$,
 Rw : $[\{\sum w(F_o - F_c)^2\} / \sum w F_o^2]^{1/2}$, where w is a weight.

* : Fourth-order least-squares fitting was not successful.

: Fourth-order least-squares fitting was not attempted.

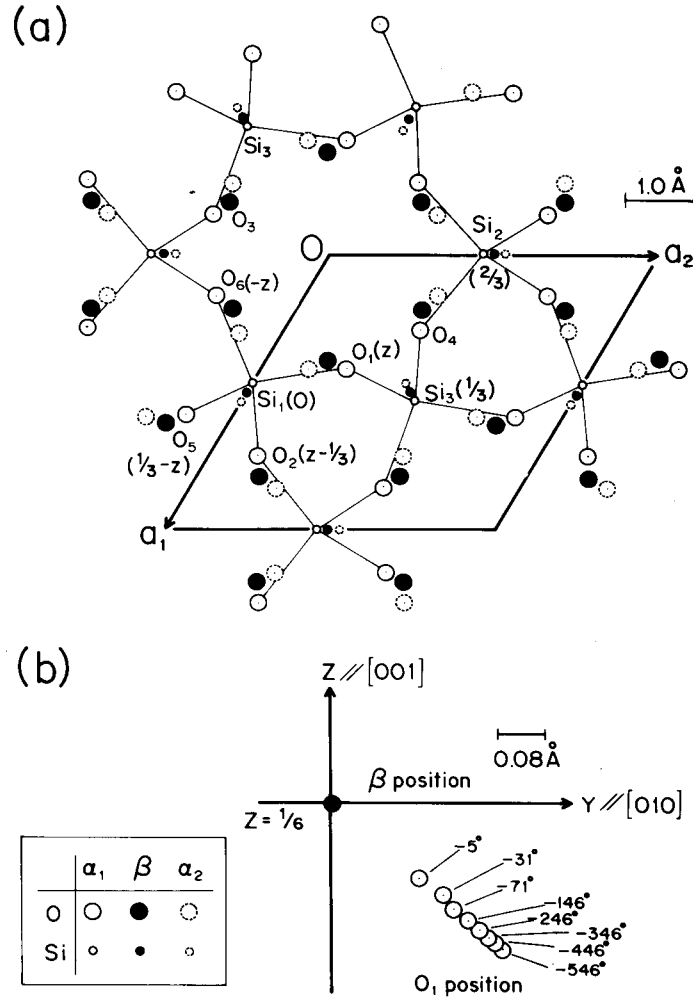


Fig. 2. Projections of atomic positions in quartz.

(a) [001] projection: two sets of α -quartz positions, α_1 and α_2 , related by Dauphiné twinning, and the β -quartz positions are indicated. Heights along [001] are shown in parentheses.

(b) [210] projection of atom O_1 at different temperatures. Temperatures are shown as $T-T_0$, T_0 is the transition temperature.

where I' and I are, respectively, the observed and corrected intensities and $a = x/(1-2x)$, x being the fraction of the sample in the twinned position. The best fit was obtained with $x = 0.005$ at 298 K – 697 K, with 0.01 at both 773 K and 813 K, and with 0.035 at 838 K. The small amount of the crystal in the twinned position might be produced at the surface by strong grinding. The increasing trend of the twinned fraction with increasing temperature is concordant with recent electron-microscope observations. According to Yamamoto *et al.* (1988),

Dauphiné twin domains are rarely observed in synthetic crystals at room temperature, but, upon heating in the electron microscope, twin domains of 500 Å suddenly appear near T_0 . The increase of x at 838 K may correspond to the beginning of *sudden* twin-domain formation. The following discussion is for twin-corrected structure amplitudes.

Although natural quartz with milky appearance has been reported to be free of significant extinction (Young, 1962; Wright and Lehmann, 1981), this is not the case for the

present specimen ; the largest reduction factor is 0.21 for reflection 011 at 298 K. However, the intensities of these lower-angle reflections appear to be satisfactorily corrected with the present extinction model. As a check, the refinement was repeated after removing these strong reflections, but no significant difference was found in the result. Structure factor tables are not reproduced here, but are available on request from the author.

The 2G refinement (Table 2) provided residual factors, R , varying from 0.02 to 0.03 through the experimental temperature range. The 4G refinement significantly improved the R -values at high temperatures. At room temperature, the use of such a model is hardly justified on the grounds of improving the fit to the experimental data ; moreover, it led to a highly complex PDF contour map fringed with negative values, probably due to overestimation of the higher-order coefficients.

β -quartz

The split-atom (SP) model was first refined with the assumption of Gaussian PDFs around each half-occupied atomic site. Then the model favoured by Young was refined in the expansion to second-order terms (2G) and, finally, up to fourth-order terms (4G) in the Gram-Charlier expansion. The SP refinement involving 16 variables (silicon atoms on positions with site symmetry 2 along $\langle 100 \rangle$ and oxygen atoms on general positions) converged smoothly, but the parameters were subject to strong inter-correlations in some cases. The R -index increased from 0.023 to 0.033 with rising temperature.

The 2G refinement with 10 variables (silicon atoms on 222 and oxygen atoms on 2 along $\langle 210 \rangle$) gave R values ranging from 0.031 to 0.040. In the 4G model, 20 independent variables are allowed by symmetry for third- and fourth-order terms. The refinement smoothly led to R values ranging from 0.021 to 0.028 with 11 to 12 non-zero higher-order coefficients for oxygen, but essentially all zero coefficients for silicon. Since the results were scarcely dependent on temperature, the 4G refinement was carried out only at some selected temperatures.

The 4G refinement provided significantly lower R 's than the 2G or SP refinements ; for

example, R for 152 observations at 848 K was improved from 0.0276 ($R_w = 0.0379$) for 16 variables in the SP refinement to 0.0244 (0.0314) for 23 variables. Thus the 4G model appears to be significantly better for describing the PDFs in detail.

Results and discussion

The structural parameters obtained from 2G refinement of α - and β -quartz are listed in Table 3. The results of split-atom refinement of the β -quartz structure are shown in Table 4, together with Wright and Lehmann (1981)'s corresponding values for comparison. The values from 4G refinement, including higher-order coefficients, are not reproduced here, but are available from the author on request.

Comparison of the structure parameters given by different authors for the α -quartz structure at room temperature

The previous structural data at room temperature (Young and Post, 1962 ; Zachariasen and Plettinger, 1965 ; Le Page and Donnay, 1976 ; Levien *et al.*, 1980 ; Wright and Lehmann, 1981 ; Lager *et al.*, 1981), show good agreement with each other as regards the positional parameters, but are definitely worse for the thermal parameters. In Table 5, two sets of parameters taken from the literature, one from X-ray and the other from neutron diffraction data, are compared with our results. A common feature in thermal parameters given by different authors, except Levien *et al.*, is that, for silicon, U_{22} is smaller than either U_{11} or U_{33} , and, for oxygen, U_{11} is considerably larger than U_{22} or U_{33} . Our results appear to confirm such a situation (in the work by Levien *et al.*, U_{22} 's for silicon and oxygen are both too large). The thermal parameters given by the two neutron diffraction studies (Wright and Lehmann, 1981 ; Lager *et al.*, 1981) are also compatible with this sequence of magnitudes. However, the values given by Wright and Lehmann are much smaller than by Lager *et al.*, who have given nearly equal magnitudes to those obtained by X-ray refinement.

All the earlier refinements were carried out on direct observations without TDS correction. This may cause artificial reduction of the ther-

Table 3. Atomic parameters and extinction coefficients (g') for the second-order refinements of quartz.

(1) α -quartz										
	298K	398K	498K	597K	697K	773K	813K	838K		
g'	2.8(2)	2.5(1)	1.9(1)	0.8(1)	0.8(1)	0.8(1)	0.7(1)	0.3(1)		
Si	x	4697(1)	4709(1)	4723(1)	4740(1)	4764(1)	4791(2)	4816(2)	4855(2)	
	b ¹¹	80(2)	105(2)	124(2)	148(2)	176(3)	198(3)	219(3)	237(4)	
	b ²²	61(3)	81(3)	98(2)	117(2)	135(3)	152(4)	172(4)	192(4)	
	b ³³	45(2)	57(2)	67(1)	82(2)	95(2)	107(2)	118(2)	123(2)	
	b ²³	-3(2)	-2(2)	-3(1)	-1(2)	-1(2)	-2(2)	4(2)	3(2)	
oxy.	x	4133(3)	4138(4)	4141(3)	4149(4)	4157(4)	4159(5)	4173(5)	4174(5)	
	y	2672(3)	2654(3)	2630(3)	2600(3)	2555(4)	2503(5)	2474(5)	2397(5)	
	z	1188(2)	1206(2)	1224(2)	1246(2)	1281(3)	1321(3)	1363(3)	1422(4)	
	b ¹¹	179(5)	232(6)	282(5)	334(6)	394(9)	451(11)	487(11)	515(13)	
	b ²²	130(5)	175(6)	208(5)	260(6)	316(7)	364(10)	417(10)	481(12)	
	b ³³	85(3)	109(3)	131(3)	162(3)	196(4)	233(5)	262(5)	302(5)	
	b ¹²	102(4)	134(5)	162(4)	195(5)	228(6)	262(8)	286(8)	312(10)	
	b ¹³	-26(3)	-32(4)	-39(3)	-43(4)	-50(5)	-51(6)	-48(6)	-48(7)	
	b ²³	-41(3)	-54(3)	-68(3)	-86(4)	-113(5)	-133(6)	-150(6)	-182(7)	
(2) β -quartz										
	848K	854K	859K	869K	891K	920K	972K	1012K	1078K	1126K
g'	0.6 (1)	0.8 (1)	0.9 (1)	1.0 (1)	1.3 (2)	2.1 (2)	4.4 (4)	3.7 (4)	2.9 (3)	2.4 (2)
silicon										
b ¹¹	279(5)	278(5)	279(5)	278(6)	279(5)	285(6)	278(7)	296(7)	307(6)	308(6)
b ²²	212(6)	214(6)	218(6)	218(7)	222(6)	222(7)	218(8)	231(8)	239(7)	238(7)
b ³³	132(3)	131(3)	133(3)	132(3)	135(3)	138(4)	138(4)	145(4)	147(4)	157(4)
oxygen										
x	4152 (8)	4157 (8)	4153 (8)	4155 (9)	4155 (9)	4149 (9)	4159 (11)	4150 (11)	4157 (10)	4156 (11)
b ¹¹	521 (18)	533 (18)	529 (17)	537 (19)	554 (18)	560 (19)	581 (22)	618 (25)	635 (21)	681 (27)
b ²²	576 (15)	577 (15)	572 (15)	577 (16)	578 (15)	579 (16)	571 (18)	595 (19)	604 (17)	637 (20)
b ³³	388 (7)	383 (7)	382 (7)	387 (8)	388 (7)	386 (8)	394 (9)	401 (9)	405 (8)	424 (8)
b ²³	-269 (11)	-261 (11)	-258 (11)	-263 (12)	-259 (11)	-252 (12)	-254 (14)	-249 (14)	-256 (13)	-268 (14)

Positional parameters x, y and z and temperature factors b_{ij} multiplied by 10^4 . For b_{ij} , see text. Esd's are in parentheses.

Table 4. Atomic parameters for split-atom refinement of β -quartz.

silicon						
	x	U_{11}	U_{22}	U_{33}		
*	0.4965(37)	0.0266(7)	0.0211(6)	0.0204(5)		
**	0.5(fixed)	0.0250(6)	0.0196(7)	0.0178(6)		
oxygen						
	x	y	z			
*	0.4169(8)	0.2385(20)	0.1402(13)			
**	0.4168(4)	0.2380(12)	0.1408(11)			
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
*	0.0509(14)	0.0390(35)	0.0351(26)	0.0303(14)	0.0046(14)	0.0120(18)
**	0.0536(9)	0.0406(23)	0.0377(24)	0.0308(7)	0.0057(8)	0.0169(14)

* : This study, at 859 K

** : Wright and Lehmann (1981), at 863 K for a natural crystal

Esd's are given in parentheses.

mal parameters (Willis and Pryor, 1975). Since our data have been corrected for TDS, the thermal parameters should be larger than the corresponding data in the literature ; in fact, they are roughly 10 % larger than the corresponding parameters reported by Le Page and Donnay (1976).

Temperature dependence of the atomic positions

Our atomic coordinates at higher temperature are very different from the corresponding ones of Young (1962), who has smoothly connected his high-temperature data to those at room temperature given by Young and Post

Table 5. Comparison of structure parameters in the present and selected earlier refinements of quartz at room temperature (in the harmonic approximation).

This study		Levien et al. (1980)*		Wright and Lehmann (1981)**	
	Si	O	Si	O	
x	0.4697(1)	0.4132(3)	0.4697(1)	0.4135(3)	0.4701(1)
y	0	0.2673(3)	0	0.2669(2)	0
z	0	0.1189(2)	0	0.1191(2)	0
U_{11}	A^2	0.73(2)	0.85(2)	1.74(6)	0.56(2)
U_{22}		0.56(3)	0.72(2)	1.32(5)	0.39(2)
U_{33}		0.66(3)	1.24(5)	0.73(3)	1.23(5)
U_{12}	$U_{22}/2$	0.94(4)		0.97(5)	0.78(1)
U_{13}	$U_{23}/2$	-0.30(4)		-0.29(4)	-0.30(1)
U_{23}		-0.03(2)	-0.47(4)	-0.00(1)	-0.41(4)
R		0.017 (267 refl.)	0.016 (194 refl.)	0.019 (204 refl.)	

* Natural crystal, X ray diffraction (Ag K_{α})** Synthetic crystal, neutron diffraction ($\lambda = 0.723$ Å)

Thermal parameters are expressed in the form:

$$T = \exp [-2 \pi^2 (h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2 h k a^* b^* U_{12} + 2 h l a^* c^* U_{13} + 2 k l b^* c^* U_{23})] \text{ , and multiplied by } 100.$$

(1962). However, the values given by the latter authors are notably different from those due to other authors.

With increasing temperature, the mean positions of oxygen and silicon atoms (α_1 -sites) move along the lines joining the corresponding Dauphiné-twin related sites (abbreviated as $[\alpha_1\alpha_2]$) towards the midpoints, which were considered as β -positions by Young (1962). For silicon, the $[\alpha_1\alpha_2]$ lines are coincident with the

two-fold axes along $\langle 100 \rangle$, and, for oxygen, they make constant angles of about $41\text{--}42^\circ$ with $[001]$ on $\{100\}$. Fig. 2(b) displays the position of the oxygen atom changing as a function of temperature. For β -quartz, the atomic mean positions show no significant change with temperature. Bond distances and angles calculated from the mean positions of atoms are given in Table 6.

Table 6. Bond lengths (Å) and angles ($^\circ$). Esd's are indicated with suffixes.

α quartz								
	298 K	398 K	498 K	597 K	697 K	773 K	813 K	838 K
O_1 -Si	1.605 ₂	1.605 ₂	1.605 ₂	1.602 ₂	1.598 ₂	1.596 ₃	1.600 ₃	1.597 ₄
O_2 -Si	1.614 ₂	1.611 ₂	1.609 ₂	1.608 ₂	1.606 ₂	1.604 ₂	1.594 ₃	1.591 ₄
Si-O-Si	143.6 ₁	144.2 ₁	144.9 ₂	145.8 ₂	147.1 ₂	148.3 ₂	149.6 ₂	151.1 ₃
O_1 -Si-O ₂	110.5 ₁	110.5 ₁	110.5 ₁	110.4 ₁	110.3 ₁	110.4 ₂	110.2 ₂	110.3 ₃
O_1 -Si-O ₆	108.9 ₁	108.9 ₁	108.7 ₁	108.6 ₁	108.5 ₁	108.3 ₂	108.5 ₂	108.2 ₃
O_1 -Si-O ₅	108.8 ₁	108.9 ₁	109.0 ₁	109.1 ₁	109.2 ₁	109.4 ₂	109.4 ₂	109.7 ₃
O_2 -Si-O ₅	109.3 ₁	109.2 ₁	109.2 ₁	109.2 ₁	109.2 ₁	108.9 ₂	109.0 ₂	108.7 ₃
β quartz								
	848 K	891 K	**		848 K			
O-Si	1.588 ₃	1.588 ₃	O_1 -Si	1.62 ₂				
*	1.620	1.624	O_2 -Si	1.58 ₂				
Si-O-Si	153.3 ₃	153.4 ₃	Si-O-Si	150 ₂				
*	145.1	144.2	O_1 -Si-O ₂	110.2 ₅				
O_1 -Si-O ₂	111.1 ₁	111.0 ₁	O_1 -Si-O ₅	109.8 ₅				
*	117.6	118.3	O_1 -Si-O ₆	105 ₂				
O_1 -Si-O ₆	107.2 ₂	107.3 ₂	O_2 -Si-O ₅	112 ₂				
*	99.6	98.8						
O_1 -Si-O ₅	110.1 ₁	110.1 ₁						
*	111.7	111.9						

For β -quartz, intermode separations or angles estimated using PDF maps calculated with coefficients from fourth-order refinement are tabulated on lines marked with single asterisks. Distances and angles calculated with the results of split-atom refinement at 891 K are shown in the column headed by a double asterisk.

Temperature dependence of the orientation of Si-O-Si planes and thermal ellipsoids

Thermal vibration is highly anisotropic for both silicon and oxygen. Young (1962) has noted that the principal axes of the thermal ellipsoids cluster around some fixed directions which show no definite temperature dependence. In the present study, however, temperature dependence of the ellipsoid orientation is clearly indicated in α -quartz, while the ellipsoids in β -quartz keep a fixed orientation. Since a detailed analysis of the temperature dependence of the ellipsoid orientation in α -quartz seems to provide important information, not only about its own structure, but also about the β -quartz structure, it is more fully discussed below.

The principal axes of the thermal ellipsoids will be called axis 1, 2 or 3 in the sequence of decreasing magnitude. In α -quartz, the silicon thermal ellipsoid has axis 1 along $[\alpha_1-\alpha_2]$, and axis 3 nearly along the Si-Si vector of the Si-O-

Si bonding plane. On the other hand, axes 1 and 2 of the oxygen ellipsoid rotate around axis 3, while the latter changes its orientation between room temperature and the transition point with a rather smaller angle.

A reference system of three orthogonal unit vectors, $\mathbf{p}$, $\mathbf{q}$ and $\mathbf{r}$, can be conveniently used to show the orientation of the Si-O-Si plane, as defined by Young (1962) :

$\mathbf{p}$ is in the Si-O-Si plane and perpendicular to the Si-Si line ;

$\mathbf{q}$ is normal to the Si-O-Si plane ;

$\mathbf{r}$ is parallel to the Si-Si line.

Fig. 3 shows the stereographic projection of the related directions for the O_1 atom (Fig. 2). The $[\alpha_1-\alpha_2]$ line virtually does not change its orientation, as already mentioned, and is thus represented with a point. A close relationship is apparent between the orientation of the oxygen ellipsoid and the Si-O-Si plane : axis 1 corresponds to $\mathbf{q}$, axis 2 to $\mathbf{p}$ and axis 3 to $\mathbf{r}$. This relationship might reflect the librational character of oxygen thermal motion around the Si-Si

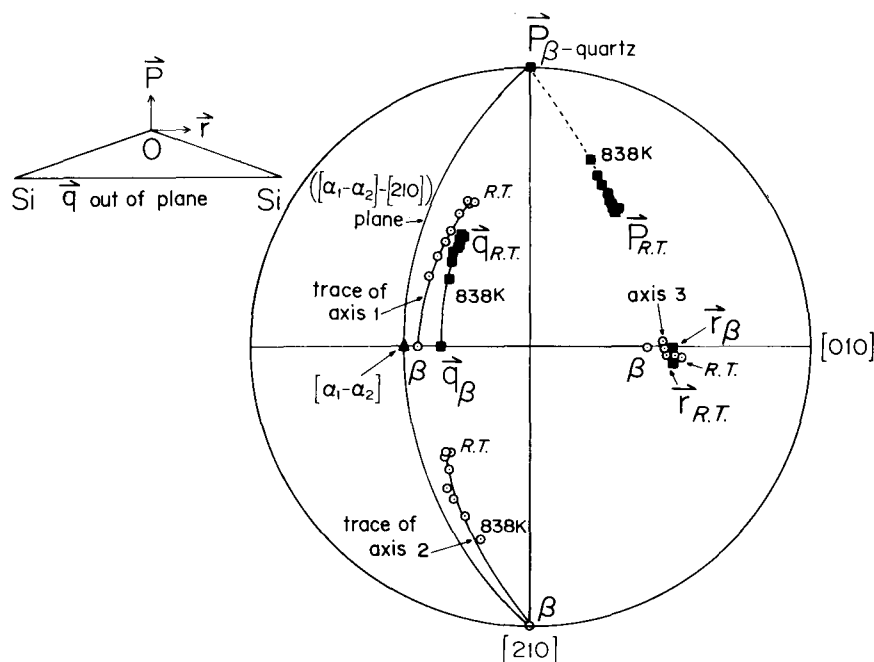


Fig. 3. Stereographic projection of the principal axes of the O_1 thermal ellipsoid, vectors $\mathbf{p}$, $\mathbf{q}$ and $\mathbf{r}$, and a plane. Vectors $\mathbf{p}$, $\mathbf{q}$ and $\mathbf{r}$ representing the special directions for the $Si_1-O_1-Si_3$ bonding plane, as illustrated in the upper left corner, are shown by solid squares. For $\mathbf{r}$, only the positions for room temperature (RT) and β -quartz (β) are shown. The principal axes, 1, 2 and 3, are plotted using open circles joined by lines. A vector $[\alpha_1-\alpha_2]$, which is almost independent of temperature, is indicated by a solid triangle. A plane formed by $[210]$ and $[\alpha_1-\alpha_2]$ is shown as $([\alpha_1-\alpha_2]-[210])$.

line. However, these related directions (*e.g.* axis 1 and **q**) do not exactly coincide and their temperature dependence is also a little different. On the stereographic projection, **q** rotates quite a small angle around **r** when the temperature is raised to a few degrees below the transition point. On the other hand, axis 1 of the oxygen ellipsoid rotates a larger angle around axis 3. This disagreement suggests that the vibration of oxygen in α -quartz might be affected by some factors other than pure libration. The thermal motions are more precisely described in terms of anharmonic potentials (see below).

Mean-square displacements of atoms and their temperature dependence

The MSDs along axes 1, 2 and 3 for oxygen and silicon, obtained from the 2G refinement, are plotted against temperature in Fig. 4. In α -quartz, the MSDs change smoothly, but not linearly. Their rates of increase become larger at higher temperature. The two smaller MSDs for oxygen reach almost the same magnitudes as the corresponding ones in β -quartz at the transition, whereas that along axis 1 shows a considerably larger gap at the transition.

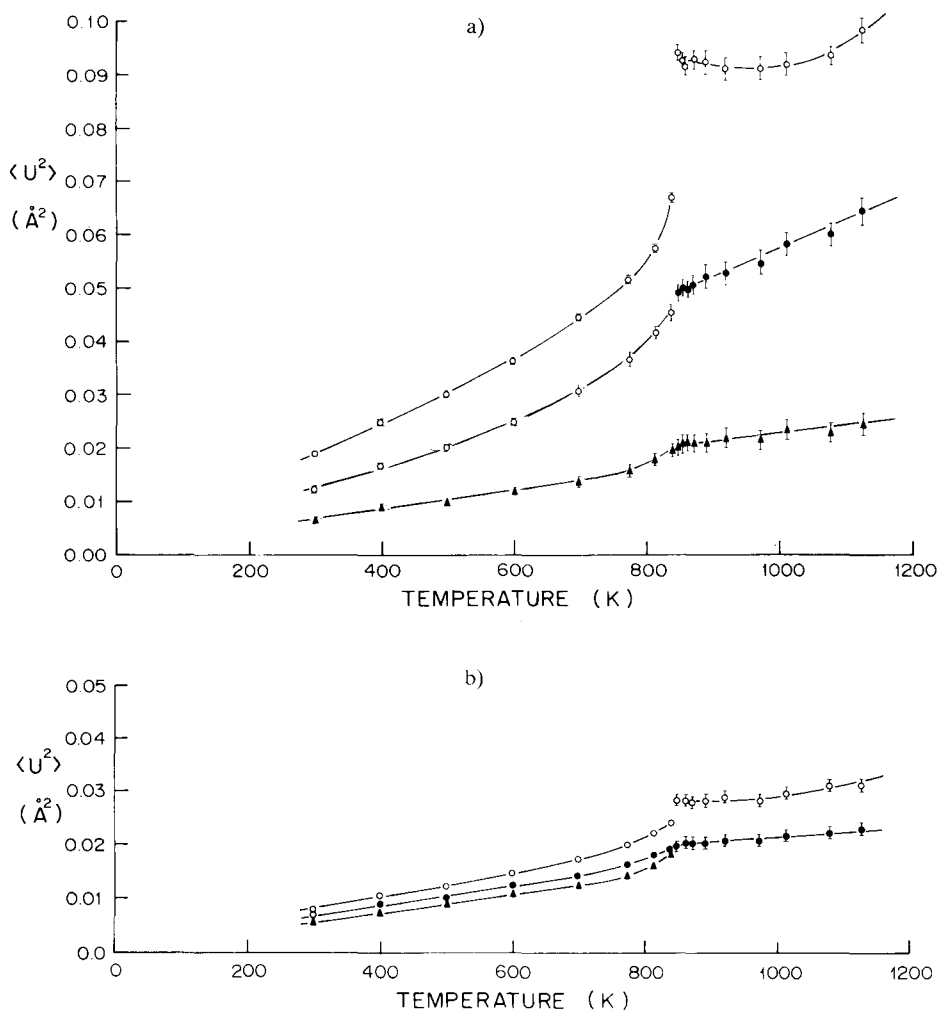


Fig. 4. Mean-square displacements along the three principal axes 1, 2 and 3 of the thermal-motion ellipsoids in quartz, (a) for oxygen and (b) for silicon. In α -quartz, axes 1 and 2 change direction with temperature. Error bars correspond to estimated standard deviation.

In β -quartz, the MSD vs. T relationships for axes 2 and 3 of the oxygen and silicon ellipsoids are well approximated by straight lines. On the other hand, the temperature dependence of the MSD along axis 1 for oxygen is quite marked. With rising temperature, it first decreases until about 950 K, and then gradually increases. This remarkable behaviour was not evident in previous studies, but these did not extend above 950 K. Similar behaviour is also observed for silicon. Some compounds having soft-mode transitions show an apparently similar temperature dependence of MSD above the transition temperature (Sakata et al., 1980), which has been interpreted by Mair (1982) as being contributed by soft modes. The temperature dependence of the MSD in quartz may invite further study on its nature.

PDFs of atoms in α -quartz

The PDF for oxygen at selected temperatures, calculated with the values obtained in the 4G refinement, are displayed in Fig. 5. Here, (1) to (5) represent the $([\alpha_1-\alpha_2]-[210])$ section at 298, 498, 697, 773 and 813 K, respectively, and (6) for the (100) section at 813 K, all passing through the mean of the PDF.

In α -quartz, the oxygen PDF contours in the immediate vicinity of the maximum are elliptical with the longer axis making an angle of about $50-60^\circ$ with $[\alpha_1-\alpha_2]$. This direction is named here for convenience the *primary direction of vibrations*. At room temperature, this direction coincides with axis 1 of the oxygen ellipsoid. At higher temperature, the outer contour lines are no longer elliptical, and this causes the *ridges* in the PDF contour maps to curve as indicated with dotted lines in Fig. 5; the ridge departing from the top along the primary direction appears to split into two, and each branch can be seen to change continuously its direction towards $-[210]$ and $[\alpha_1-\alpha_2]$, respectively. The ridge turning to $[\alpha_1-\alpha_2]$ becomes clearer with increasing temperature. At 813 K, the PDF is already not zero at the α_2 site.

This characteristic feature of PDF contour maps at different temperatures can be interpreted as follows. An oxygen atom, if it is moving in the immediate vicinity of the equilibrium position, might prefer to move along $\mathbf{q}$, as expected from pure librational motion of the

Si-O-Si plane, and also towards the larger open space in the $-[210]$ direction (see Fig. 2); in such a PDF map, these two directions could not be resolved at the central part, thus forming the primary direction between $\mathbf{q}$ and $-[210]$ as a composite effect. Hence, the primary direction is considered to be less temperature-dependent than $\mathbf{q}$, and hardly free to change its orientation. (Vector $\mathbf{q}$ changes its orientation only about 15° from 298 K to 838 K). At higher temperature, the atom is subjected to vibrations of greater amplitude and must find another site of potential mini-

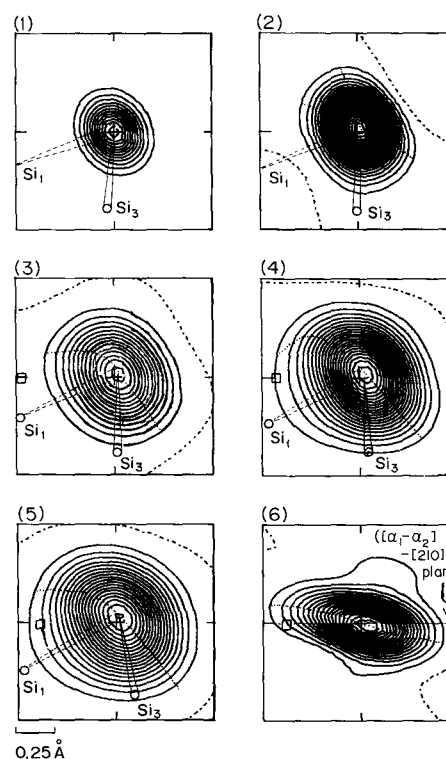


Fig. 5. Probability density function for O_1 in α -quartz, with silicon atoms projected on the sections. Crosses show atom positions in higher-order refinements.

(1) to (5) are the sections of the $([\alpha_1-\alpha_2]-[210])$ plane (See Fig. 3) at different temperatures with $[\alpha_1-\alpha_2]$ lines in the horizontal direction and $[210]$ vertical. (6) is the (100) section. α_2 sites are shown by open squares. Dotted lines crossing contours are to indicate ridges of contour maps. (1): 298 K; (2): 498 K; (3): 697 K; (4): 773 K; (5) and (6): 813 K. Contour intervals are 4.0, 1.0, 1.0, 0.5, 0.5 and $0.5 \text{ \AA}^{-3}$, respectively. Zero contours are indicated by broken lines.

imum coinciding with the α_2 site, towards which the atom can move more easily. This effect of the α_2 site is also shown in a different section for the 813 K case in (6) of Fig. 5.

At 813 K, the α - β transition has not yet taken place, but there is already a substantial presence of oxygen atoms in the α_2 site. Some small fraction of the crystal may fail to revert to the original orientation, resulting in Dauphiné twinning. At temperatures nearer the transition, the fraction of the sample in the twinned position increases rapidly.

The structure of β -quartz

In the disordered model, each atom is assumed to move about either the α_1 or the α_2 site (static disorder), or to oscillate over the two sites (dynamic disorder). Therefore, we can define the vector $[\alpha_1-\alpha_2]$ as in α -quartz, and it seems reasonable to assume that this vector holds the same orientation as in α -quartz (as noted above, the $[\alpha_1-\alpha_2]$ orientation remains fixed in the α -quartz structure). If a conventional second-order refinement is applied to such a disordered structure, one may have highly anisotropic thermal ellipsoids with major axes on the $[\alpha_1-\alpha_2]$ vectors. However, as indicated in Fig. 3, our axis 1 of the oxygen ellipsoid is not coincident with $[\alpha_1-\alpha_2]$, but rather oriented towards the $\mathbf{q}$ -vector.

In order to explain the present diffraction data, the double minimum model must be modified so that the excess potential between the minima vanishes or is low enough to allow the atoms to move more freely through the midpoints. For the oxygen atom, such motion must be librational and may cause axis 1 of the ellipsoid to deviate from $[\alpha_1-\alpha_2]$ towards the $\mathbf{q}$ vector. Thermal vibration for oxygen, as in Liebau and Böhm (1982)'s interpretation of the β -quartz structure, may be practically librational because the authors adopted a dynamical stand-point.

The PDF for oxygen (Fig. 6) is eventually unimodal at all temperatures, but deviates considerably from a Gaussian distribution; the mode of the oxygen PDF is situated on the two-fold axes parallel to $\langle 210 \rangle$, but is shifted about 0.13–0.18 Å from the mean (indicated at the centres of the maps and also given in Table 4) towards $-\langle 210 \rangle$. The PDF for silicon is also clearly anisotropic with axis 1 in $\langle 100 \rangle$, but it is

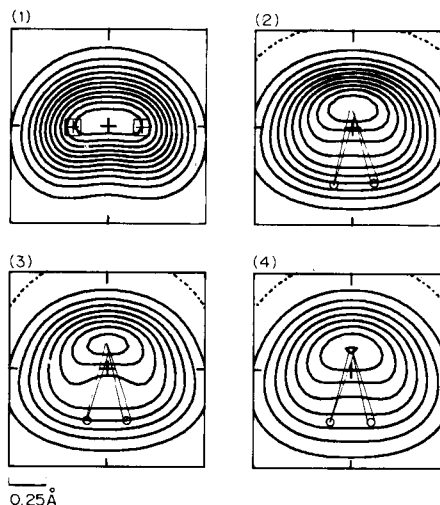


Fig. 6. Probability density functions for O_1 in β -quartz, with silicon atoms projected on sections of the plane including the major axis (horizontal) of the thermal ellipsoid and the two-fold axis along $[210]$ (vertical). Zero contours are indicated by broken lines. Contour interval is $0.5 \text{ \AA}^{-3}$.

(1) : 848 K, from split-atom refinement for comparison; open squares show refined positions.

(2) : 848 K; (3) : 859 K; (4) : 1078 K.

The central crosses in (2) to (4) show atom positions in higher-order refinements.

well approximated by a Gaussian-type distribution. These characteristic features of the PDFs could be at least qualitatively accounted for in terms of librational motion of the oxygen atoms and oscillatory motion of the silicon atoms along $\langle 100 \rangle$. Motions of both kinds of atoms could be correlated with each other to relieve structural distortion. Fig. 7 shows such a correlated displacement pattern; this correlation may be compatible with the B_1 symmetry (Axe and Shirane, 1970). In these motions, the oxygen and silicon atoms are assumed to occupy simultaneously the positions denoted by β , and to be displaced together towards position 1 or 2 as indicated by arrows. In such a case, the mean position of the oxygen PDF should not be coincident with position β , but rather displaced towards the positive direction of $\langle 210 \rangle$. Position β for oxygen is not exactly the same as Young's (1962), because of its displacement from the midpoint of the line joining position 1 and 2. Our mode positions on the PDF maps (Fig. 6) may represent β positions in librational motion.

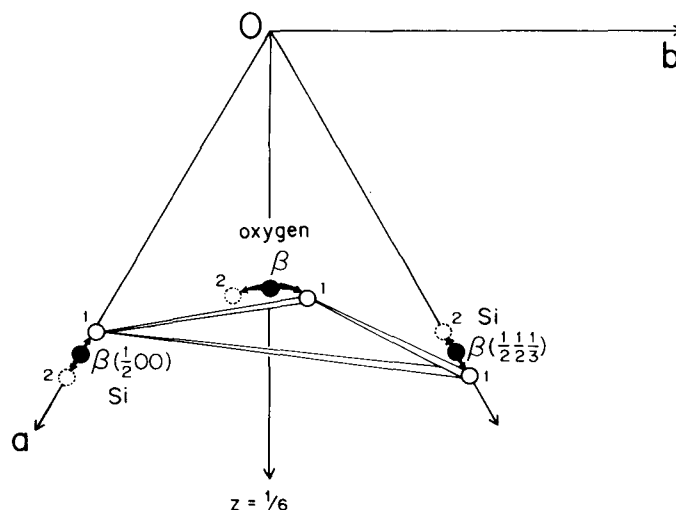


Fig. 7. A (001) projection of a possible displacement pattern of silicon and oxygen atoms in β -quartz. Three positions for each atom site are connected by heavy arrows to indicate the displacements. Positions 1 and 2 for oxygen correspond to α_1 and α_2 , respectively, but do not exactly coincide with them. A $\text{Si}_1\text{-O}_1\text{-Si}_3$ triangle is illustrated.

In his application of the Edgeworth expansion to structural studies, Johnson (1970) has found that intermode distances tend to give more reasonable bond lengths than intermean distances when large thermal libration effects are present. Three kinds of distance have been compared for the C-H bond in photodimer of isophorone; i.e. the corrected intermean separation with a *riding on rigid-body* model, the uncorrected intermean separation and the intermode separation. Johnson found the intermode distance to be in better agreement with the spectroscopically determined value. Similarly, in quartz, an intermode separation may provide a more realistic estimation of the bond length than an intermean separation. We may take such an intermode separation as the distance between the β positions for silicon and oxygen.

Although, in general, mode positions cannot be determined with the same precision as mean positions, we attempt here to determine the atomic mode positions in β -quartz; the intermode distances and angles are given in Table 6, together with the corresponding values for mean positions. The intermode distances Si-O and angles Si-O-Si are, respectively, about 1.62 Å and 144-145°, which are slightly longer than or about equal to those in α -quartz. On the other hand, the distances obtained from the SP refinement (Table 6) – from which we

can derive a rough estimation of the bond lengths when the atoms are somewhere between positions β and 1 (or 2) – are 1.58 and 1.62 Å, respectively. This shows a larger contraction of one of the bonds – Wright and Lehmann (1981) obtained 1.591 and 1.606 Å, respectively, from neutron diffraction data. The present values indicate that the bond length and the Si-O-Si angle must be least distorted when the atoms occupy β positions as long as only the B_1 mode vibrations are concerned. On the contrary, the tetrahedral angles O-Si-O are seriously distorted when the atoms are located on β positions. Thus, in our model of β -quartz, the structure may be stabilized by bond bending of the tetrahedra, while the Si-O-Si bonding planes are undergoing librational motion, keeping them rather rigid.

Unimodal PDFs might also result from a spatial or time average, if the atoms are disordered over the α_1 and α_2 orientations. The apparently unimodal (or weakly bimodal) PDF displayed in (1) of Fig. 6 is calculated from the parameters in the SP refinement at 848 K. The difference between the two PDF maps (1) and (2) of Fig. 6 is, however, obvious, and must correspond to the fact that the split-atom refinement has not been able to provide the best fit. If such disorder were realized in β -quartz, the split-atom model should have given the best fit to the observed structure factors.

Concluding remarks

The present X-ray diffraction study of quartz at different temperatures provides important and detailed information about the temperature dependence of the MSDs and PDFs of silicon and oxygen atoms, and enables us to formulate a model for the structure of β -quartz.

Thermal vibrations are highly anisotropic for both silicon and oxygen atoms. However, there is no clear evidence supporting the disordered model of the β -quartz structure. Instead, an ordered model (or weakly disordered model) is presented, where the oxygen atoms are assumed to undergo librational motion and silicon atoms to oscillate in correlation with the oxygen motion. In this model, the Si-O length and the Si-O-Si angle remain nearly equal to those in α -quartz.

On increasing the temperature in β -quartz, the MSDs of oxygen and silicon atoms show anomalous behaviour, apparently related to the α - β transition.

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