

## Study of $\beta$ -Quartz by Neutron Multiple Diffraction\*

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(Received 3 July 1992; accepted 18 August 1993)

### Abstract

A study of the crystal structure of  $\beta$ -quartz has been done employing neutron multiple diffraction as a method of analysis. The sample used in the measurements was a natural quartz crystal shaped into an orthocylinder of size 5 cm diameter  $\times$  5 cm height with the crystallographic direction [00.1] parallel to the cylinder axis. An experimental primary-beam multiple diffraction pattern was obtained with the  $\beta$ -quartz 00.1 space-group-forbidden reflection. To obtain the  $\beta$ -phase, the sample was heated to 1003 K inside an electrical furnace specially designed for the experiment. Theoretical *Umweganregung* primary-beam multiple diffraction patterns were calculated for both an ordered and a disordered model of the  $\beta$ -quartz structure and compared to the experimental pattern. The agreement between patterns was verified by calculating the reliability factor  $R = \sum_k |I_k(\text{obs.}) - CI_k(\text{calc.})| / \sum_k I_k(\text{obs.})$ , where  $I_k(\text{obs.})$  and  $I_k(\text{calc.})$  are, respectively, observed and calculated integrated intensities. The variation of the scale factor  $C$  allowed the determination of a minimized  $R$  factor for each model of the structure. The  $R$  factor found for the disordered model was 3.3% lower than that calculated for the ordered model, namely  $R = 0.110$  and  $R = 0.143$ . No parameters were refined in this analysis.

### Introduction

$\alpha$ -Quartz, one of the polymorphs of silica ( $\text{SiO}_2$ ) that is stable at room temperature, has a structure described by either of the two enantiomorphic trigonal space groups  $P3_121$  or  $P3_221$  (Wyckoff, 1965). At approximately 846 K,  $\alpha$ -quartz undergoes a reversible transition to  $\beta$ -quartz with minor changes in the silicon and oxygen positions.  $\beta$ -Quartz has a structure with hexagonal symmetry in either of the two enantiomorphic space groups  $P6_222$  or  $P6_422$  (Wyckoff, 1965). Both  $\alpha$ - and  $\beta$ -quartz have three

molecules in hexagonal unit cells with almost the same dimensions.

In a study dealing with the mechanism of the  $\alpha$ - $\beta$  phase transition in quartz, Young (1962) employed X-ray diffraction to analyze the structures of both phases at high temperatures. His study was made in terms of the positions of the silicon and oxygen atoms related to a configurational potential energy having a single or a double minimum. According to this author, a double minimum exists in the  $\alpha$  phase. In the  $\beta$  phase, three possible situations were likely to occur: (1) the atoms might be statistically distributed over two minima in the configurational potential energy and constrained to vibrate primarily within a single minimum; (2) the atoms might be statistically distributed but have sufficient thermal energy to vibrate freely between the two minima; (3) the two minima might be replaced by a single broad minimum centered at the ideal  $\beta$ -quartz positions. As pointed out by Young, hypotheses (1) and (2) could only be distinguished by magnetic resonance methods but, in principle, accurate and extensive X-ray data could distinguish a double- from a single-minimum case. After a detailed intensity analysis, Young verified that the single-minimum model [hypothesis (3)] was favored by the results over the double-minimum case [hypotheses (1) and (2)]. The ordered model of structure suggested by Young for  $\beta$ -quartz is the same as that proposed by former authors (see Wyckoff, 1965) where the silicon and oxygen atoms occupy, respectively, the special positions 3(c) and 6(f) in either of the above-mentioned enantiomorphic hexagonal space groups.

Wright & Lehmann (1981), employing high-resolution neutron diffraction data obtained from powdered synthetic quartz and single crystals of synthetic and natural quartz, studied the  $\alpha$ - and  $\beta$ -quartz structures. The authors verified that for  $\beta$ -quartz the best agreement between the experimental intensity data and theoretical calculations was accomplished when a disordered structure was considered. In particular, the single-crystal data refinements showed that disorder should be assumed only for the oxygen atoms since, for silicon, they indicated a perfectly isotropic thermal motion. For

\* Research partially supported by a SUBIN-CNPq-SBCr covenant under contract no. 065/82.

† Work supported by a fellowship granted by FAPESP.

oxygen, the atomic density was strongly smeared along a line connecting two possible sites in a twinned  $\alpha$ -quartz structure. These two sites are symmetrically placed around the  $6(j)$  special positions in the ideal  $\beta$ -quartz structure. Nevertheless, in order to keep the  $\text{SiO}_4$  tetrahedra regular, a small disorder was also assumed for the silicon atoms. It was introduced as a small anisotropy in the thermal parameters for silicon. The structure obtained from the powder data refinements was essentially the same as that obtained from the single-crystal data refinements. However, an isotropic thermal parameter had to be used since the limited number of data available restricted the number of parameters in the refinement. A small disorder was also assumed for silicon. It was introduced by placing the silicon atoms in the  $6(g)$  instead of the  $3(c)$  special positions of  $P6_322$ .

In the following sections, we present a study of the crystal structure of  $\beta$ -quartz that has been done employing neutron multiple diffraction (n.m.d.) as a method of analysis. Experimental n.m.d. patterns for both primary and transmitted beams were obtained with a natural quartz crystal at 1003 K. Indexing of the patterns showed a high density of secondary reflections throughout the azimuthal angular interval of measurement characterizing, consequently, a many-beam case. To solve the problem of calculating intensities in such a case, Parente, Mazzocchi & Pimentel (1994) worked out intensity solutions suitable for any type of beam. They have written a computer program (*MULTI*) to simulate n.m.d. patterns for primary and transmitted beams. A first version of the program was particularly tailored to be applied in this study permitting the calculation of theoretical  $\beta$ -quartz n.m.d. patterns, for both an ordered and a disordered model of the structure. A description of the experimental arrangement and procedures used in the measurements, the method employed to obtain observed and calculated integrated intensities and the results of the comparison between them are presented in the following sections.

### Experimental

In order to obtain the  $\beta$ -quartz n.m.d. patterns, an experimental arrangement was assembled in the IPEN neutron diffractometer installed at the IEA-R1 2 MW research reactor. This arrangement included, besides the normal neutron diffractometer apparatus, a special collimator for n.m.d. experiments, a five-circle goniometer and an  $^3\text{He}$  detector aligned with the incident beam. This detector was installed to allow the measurement of transmitted-beam n.m.d. patterns. Fig. 1 is a scheme of the arrangement showing the disposition of the special collimator, the  $^3\text{He}$  detector and the  $\text{BF}_3$  detector normally used in the neutron diffractometer. Fig. 1 also gives an idea of the

geometry of the experiment. Three kinds of pattern are observable in the phenomenon. If the primary reflection is forbidden an *Umweganregung* (*Umweg*) pattern is obtained. This kind of pattern exhibits numerous intensity peaks above a background level. If the primary reflection is permitted an *Aufhellung* pattern is observed. It corresponds to the appearance of intensity dips in a constant primary intensity level. It should be noted that the transmitted-beam pattern is always *Aufhellung* type whether the primary beam is permitted or forbidden. A third kind of pattern, not depicted in Fig. 1, is a mixed *Aufhellung-Umweg* pattern. It occurs when the primary reflection is not forbidden but very weak.

To obtain n.m.d. patterns with good resolution, the second Soller collimator was substituted by a special collimator (Mazzocchi, 1984). This special collimator limits the angular divergence of the monochromatic beam, in both vertical and horizontal directions, to a few minutes of arc. It is actually an evolution of the collimator conceived by Parente & Caticha-Ellis (1974) to be used in n.m.d. experiments. It is constituted of 16 alternate sections of vertical and horizontal plates, each section formed by 15 equidistant parallel plates. Owing to the alternation, sections of the same type, vertical or horizontal, form discontinuous channels in the collimator. The lengths of the sections were calculated in order to hinder those neutrons that could pass through nonconsecutive channels. The distances between plates and the total length of the channels were chosen so that both vertical and horizontal angular divergences, referred to a central line along the collimator, are equal and of the order of  $10'$ .

The IPEN neutron diffractometer is normally equipped with a five-circle goniometer. This goniometer has, in addition to the axes  $\theta$ ,  $\omega$ ,  $\varphi$  and  $\chi$  of a four-circle goniometer, an extra  $\Sigma$  axis, which can be

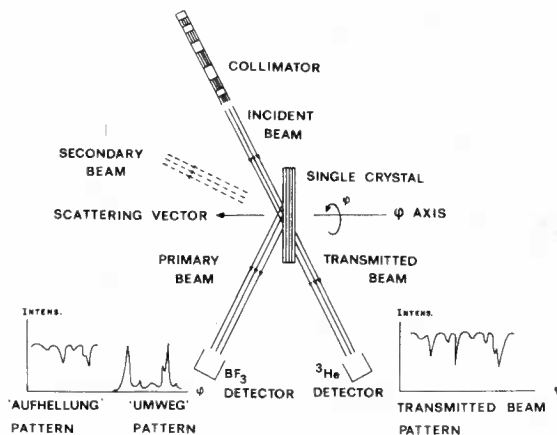


Fig. 1. Scheme of the experimental arrangement used in this work. Different types of patterns observed in primary and transmitted beams are also depicted.

set along the scattering vector of a primary reflection (Parente & Caticha-Ellis, 1974). Sample rotation around the scattering vector of a primary reflection is a necessary feature to perform Renninger scans (Renninger, 1937). Nevertheless, because parts of the structure of the goniometer intercept the incident and primary beams during a  $\Sigma$  rotation, limiting its angular range to an interval of about  $-30$  to  $+30^\circ$ , we preferred to use the  $\varphi$  axis in the measurements. This axis has no limitations in its angular range allowing for a complete turn of the crystal in any direction. Moreover, the mechanical precision attained during the making and assembling of its constituent parts is higher than in the other axes of the goniometer. To use the  $\varphi$  axis it was necessary to mount the crystal so that the scattering vector of the primary reflection became aligned with this axis.

The experimental measurements were carried out with a natural quartz crystal shaped into an orthocylinder of size 5 cm diameter  $\times$  5 cm height with the [00.1] crystallographic direction approximately parallel to the cylinder axis. To heat the crystal, an electrical furnace was designed and constructed (Mazzocchi, 1984). A simplified drawing of this furnace is shown in Fig. 2. A thin-walled stainless-steel cylindrical capsule held the crystal, which was firmly maintained in position by well compacted vitreous silica powder. Silica has a low absorption coefficient for neutrons and, in the vitreous form, has no coherent scattering. Heating was provided by a Thermocoax\* heating resistance wound around the crystal. A thermocouple placed near the resistance controlled the heating *via* a proportional temperature controller. Another thermocouple in contact with the top of the crystal measured its temperature. A thermal insulator, shown in Fig. 2

without details, was welded to the capsule to provide a thermal insulation between the furnace and the goniometer head used in the setting of the primary reflection. A thin-walled aluminium heat shield covered the capsule to reduce the air convection around it. This precaution was taken to avoid large temperature gradients in the crystal. The shield was shaped like a cup having dimensions such that its internal surfaces were kept about 1 cm from the top and cylindrical surfaces of the capsule.

To measure the  $\beta$ -quartz n.m.d. patterns, the crystal was heated to 1003 K. This temperature ensured that all the crystal was in the  $\beta$ -phase during the measurements but avoided the phase transition to high-tridymite at 1143 K (Dana & Dana, 1962). Owing to both the large dimensions of the crystal, the increase in the rate of expansion of the unit-cell volume just a few degrees below the transition temperature (Ackermann & Sorrel, 1974) and the occurrence of large temperature gradients during the temperature increase, cracking of the crystal was likely to occur near the transition temperature. To prevent cracking, a nearly constant low rate of  $0.7 \text{ K min}^{-1}$  was employed in the heating in an interval including the transition temperature, namely from 813 to 873 K. Under 813 K and over 873 K, rates were of the order of  $2 \text{ K min}^{-1}$ . In spite of such precautions, the opening of the capsule at the end of the measurements revealed a completely cracked crystal. Although the hypothesis of cracking during the heating could not be entirely discarded, it was assumed that it occurred after an accidental rupture of the resistance. Certainly, after this rupture, the crystal temperature dropped very rapidly creating the conditions for cracking. Fortunately, this unexpected ending of the experiment occurred after enough data had been obtained. Concerning the multiple diffraction phenomenon, it was verified that a crystal behaves equally no matter whether it is a single piece or broken in several pieces, provided the pieces maintain their relative orientation to each other. In fact, a comparison between 00.1 *Umweg* patterns obtained at room temperature before and after the phase transition showed no remarkable differences. They differed slightly in the spreads and intensities of their peaks. The differences were ascribed to an increase in the mosaic spread of the crystal after cracking rather than to any other disturbance in the phenomenon provoked by the cracking itself (Mazzocchi, 1984).

The 00.1 space-group-forbidden reflection was chosen as the primary reflection for the  $\beta$ -quartz measurements. Both primary- and transmitted-beam n.m.d. patterns were measured simultaneously in a  $\varphi$  scan made in steps of  $0.1^\circ$ , 3 min of counting time each step. The scan extended over an azimuthal angular interval from  $-1$  to  $85.8^\circ$  on the measuring scale. The intensity of the primary beam was observed by the

\* Thermocoax is a trademark of Sodern, Suresnes (Seine), France.

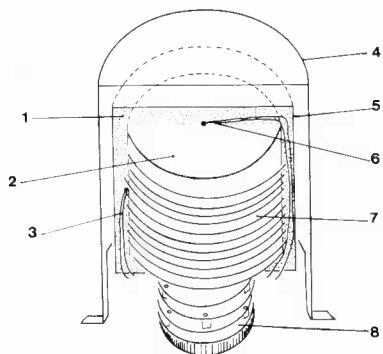


Fig. 2. Schematic view of the furnace employed in the measurements. Numbers indicate: 1 amorphous silica powder; 2 quartz crystal; 3 control thermocouple; 4 heat shield; 5 capsule; 6 measuring thermocouple; 7 heating resistance; 8 thermal insulator.

$\text{BF}_3$  detector normally used in the diffractometer. As expected, the primary-beam pattern is *Umweg* type. Simultaneously, the intensity of the transmitted beam was measured by the  $^3\text{He}$  detector. To shield this detector, a 1 mm thick cadmium foil covered it completely, except for a small circular aperture for the transmitted beam. This aperture had a diameter such that only neutrons that had traversed the crystal could reach the detector. Since the small divergence of the special collimator totally governed the experimental resolution, no collimators were used in front of both  $\text{BF}_3$  and  $^3\text{He}$  detectors. Although the transmitted-beam pattern was also adequate in the  $\beta$ -quartz structural analysis, the authors preferred to use the primary-beam pattern exclusively. [The reader can see part of the transmitted-beam pattern in the work by Parente, Mazzocchi & Pimentel (1994).]

### Results and discussion

In spite of the accidental interruption of the heating, the angular extension of the measurements was enough to show basic  $60^\circ$  patterns. Each basic pattern consists of two symmetrically opposed parts that are mirror images. The symmetry exhibited by the patterns is in agreement with the sixfold symmetry of the 00.1 primary reflection since the scattering vector for this reflection lies along the  $c$  axis of the unit cell. In a full  $360^\circ$  extension, six basic patterns appear in sequence every  $60^\circ$  from an arbitrary origin in the indexing scale (Chang, 1984).

In the early stages of the data analysis, during indexing of the experimental  $\beta$ -quartz *Umweg* pattern, it seemed that something was wrong with the experiment or even with the indexing itself. The indexing revealed a high density of secondary reflections. This was, in principle, incompatible with the experimental pattern which was formed of sparse discrete peaks. An attempt to correlate the existence of discrete peaks with the presence of stronger secondary reflections failed completely. Only when a simulated pattern was calculated by *MULTI* could it be verified that the experimental pattern and the indexing were both correct. Fig. 3 shows a small portion of the *Umweg* pattern observed for the 00.1 forbidden reflection from  $\beta$ -quartz. It includes two peaks symmetrically positioned around  $\varphi = 60^\circ$  in the indexing scale. Such a position corresponds to the ending of a basic pattern and the beginning of the next one. The high density of secondary reflections mentioned before is well illustrated in Fig. 3. It shows the indexing of the theoretical  $\beta$ -quartz pattern. The indices of all the secondary reflections contributing in the interval considered in the figure are indicated. It should be mentioned that the situation pictured in Fig. 3 is constant for the entire pattern. The 'correctness' of the theoretical intensity calculations can be evaluated in Fig. 4 by observing the agreement between part of the experimental  $\beta$ -quartz *Umweg* pattern and a corresponding simulated pattern calculated by *MULTI*. The full line corresponds to a fitting of Gaussians to the simulated pattern. The

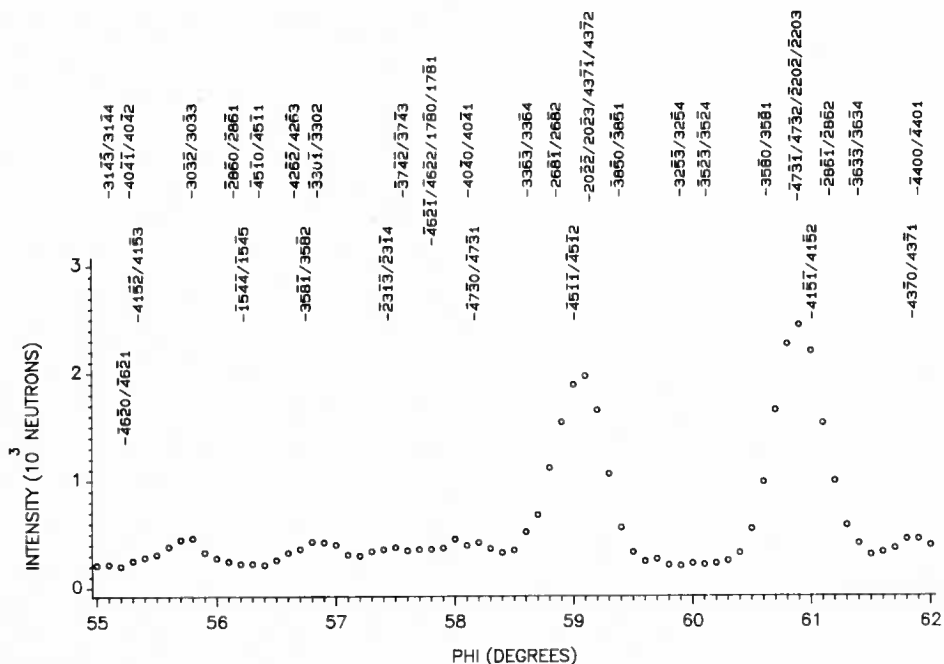


Fig. 3. Indexing of part of the experimental  $\beta$ -quartz *Umweg* pattern exhibiting a high density of secondary reflections.

patterns are normalized for the maximum intensity of the experimental peak at  $\varphi \simeq 50^\circ$ .

At this point, it is worthwhile mentioning two features of the  $\beta$ -quartz n.m.d. patterns. A first feature is the fact that the secondary reflections occur in pairs of the type  $hkl/h,k,1-l$ . This systematic double occurrence is due to the rotation of the crystal around a symmetry axis of the lattice (Cardoso, 1983), *e.g.* the sixfold symmetry axis  $c$  in the  $\beta$ -quartz lattice. Therefore, the number of beams involved in the  $\beta$ -quartz patterns is always even and equal to or greater than four, except when no multiple diffraction occurs. A second feature is, as mentioned before, the occurrence of a high density of secondary reflections. This is due to the following:

1. The Ewald sphere for the wavelength used in the measurements ( $\lambda = 1.137 \text{ \AA}$ ) has a large value when compared to the volume of the  $\beta$ -quartz reciprocal unit cell.

2. Space group  $P6_222$  (or enantiomorphic  $P6_422$ ) for both structure models imposes only a few restrictions concerning the possible reflections.

According to 1, a very large number of reciprocal-lattice points are touched by the Ewald sphere during a complete crystal rotation. Since, according to 2, most of these points correspond to permitted reflections, the result is m.d. patterns with a high density of secondary reflections throughout the entire interval of  $\varphi$ . On the other hand, it is well known that reciprocal-lattice points are not actually dimensionless for a real crystal. If the crystal is mosaic, the dimensions that can be assigned to the points are dependent on the mosaic spread which is, in general,

measured in tenths of a degree. For this reason, interactions between beams extend in an interval of  $\varphi$  that frequently exceeds  $1^\circ$ . Consequently, if a m.d. pattern presents a high density of secondary reflections, all those non-simultaneous reflections occurring in the neighborhood of a certain value of  $\varphi$  can be overlapping. This overlapping increases the number of beams participating in the phenomenon at that  $\varphi$  value. Therefore, intensity calculations for  $\beta$ -quartz had to be treated as a many-beam case. In fact, during the calculations of the theoretical patterns it was verified that, at a given  $\varphi$  value, the number of beams involved frequently exceeded 20, rarely being less than 10.

To perform the analysis, n.m.d. patterns were simulated for both an ordered and a disordered model of the  $\beta$ -quartz structure. The disordered model is one obtained by Wright & Lehmann (1981) from neutron single-crystal diffraction data refinements. In such a model, disorder is assumed only for oxygen atoms. Each oxygen atom occupies one of two 'split-half-oxygen positions' corresponding to the  $12(k)$  general positions in the space group. The silicon atoms occupy the  $3(c)$  positions. Wright & Lehmann (1981) refined structural parameters from data obtained with single crystals of natural and synthetic quartz at 863 K. They also refined parameters from powder data obtained at 903 K. However, as mentioned before, they had to use an isotropic thermal parameter for silicon in the refinement of the 903 K data. The ordered model, on the other hand, corresponds to a well known  $\beta$ -quartz structure where the oxygen atoms occupy all the  $6(j)$  special positions in the space group, instead of the partial occupation of the  $12(k)$  general positions. The silicon atoms occupy the same  $3(c)$  positions. This structure was redetermined by Young (1962) in a study of the  $\alpha$ - $\beta$  transition in quartz by means of X-ray diffraction. Using numerous specimens from a variety of sources, Young refined the structural parameters from data obtained at several different temperatures ranging from 723 to 923 K.

In the calculations of the simulated n.m.d. patterns, we preferred to use for both structure models the anisotropic thermal parameters refined by Young from data obtained at 923 K. The values refined by Wright & Lehmann for the disordered model were discarded on the assumption that the temperature they used in the measurements (863 K) is too far from that used in this work (1003 K). For the positional parameters, the values used in the simulation of the disordered model were those determined by Wright & Lehmann in the refinement of the single-crystal data obtained with a natural quartz crystal at 863 K. For the ordered model, the values correspond to the data obtained by Young at 873 K. For this temperature, Young conserved the atomic positions of the silicon atoms fixed at  $(\frac{1}{2}, 0, 0)$ , in better

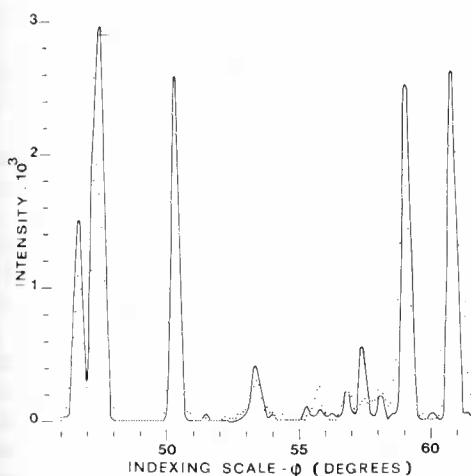


Fig. 4. Part of the experimental  $\beta$ -quartz *Umweg* pattern compared to the corresponding simulated pattern calculated for a disordered model of the structure suggested by Wright & Lehmann (1981). The full line represents the simulated pattern obtained after application of a program that adjusts Gaussians to the peaks. Patterns are normalized for the peak of higher intensity in the experimental pattern.

Table 1. Positional and anisotropic thermal parameters used in the simulations of the  $\beta$ -quartz n.m.d. patterns

Space group:  $P6_222$ .

	Anisotropic thermal parameters, both models ( $\text{\AA}^2$ ) (Young, 1962)		Positional parameters, ordered model (Young, 1962)		Positional parameters, disordered model (Wright & Lehmann, 1981)			
	Si	O	Si	O	Si	O		
$\beta_{11}$	0.0228	0.0552	x	$\frac{1}{2}$	0.20685	x	$\frac{1}{2}$	0.41684
$\beta_{22}$	0.0197	0.0460	y	0	$2x$	y	0	0.23801
$\beta_{23}$	0.0106	0.0310	z	0	$\frac{1}{2}$	z	0	0.14081
$\beta_{12}$	$\beta_{22}/2$	0.0211						
$\beta_{13}$	-0.0015	-0.0003						
$\beta_{23}$	$2\beta_{13}$	-0.0214						

Table 2. Observed and calculated integrated intensities for  $\beta$ -quartz

Observed		Calculated for the ordered model (Young, 1962)		Calculated for the disordered model (Wright & Lehmann, 1981)	
$\varphi(\text{obs.})$ ( $^\circ$ )	$I_k(\text{obs.})$	$\varphi(\text{calc.})$ ( $^\circ$ )	$I_k(\text{calc.})$	$\varphi(\text{calc.})$ ( $^\circ$ )	$I_k(\text{calc.})$
50.34	957.45	50.36	825.12	50.36	871.35
59.04	912.33	59.12	1136.16	59.13	962.93
60.90	1166.05	60.87	1103.76	60.87	943.50
69.57	809.29	69.65	164.16	69.64	832.50
84.68	246.83	84.77	416.88	84.77	274.73
88.59	405.80	88.62	848.88	88.63	419.03
91.29	344.03	91.37	432.00	91.37	452.33
95.22	256.53	95.23	181.44	95.23	321.90
103.42	439.32	103.40	378.00	103.41	505.05
104.51	585.85	104.58	794.88	104.59	740.93
110.30	1013.01	110.35	794.88	110.36	860.25
119.02	1069.15	118.85	1131.85	118.90	957.38
120.83	1006.69	120.87	1164.24	120.87	993.45
129.61	826.64	129.65	803.52	129.65	826.95

accordance with the primitive model of the structure. For other temperatures, he refined the coordinate  $x$  for the silicon atoms, resulting in values somewhat different from  $\frac{1}{2}$ . Table 1 lists the values of the parameters used in the simulations of the  $\beta$ -quartz n.m.d. patterns according to the observations made above.

The unit cell used in the calculations has the dimensions  $a_0 = 4.9977$ ,  $c_0 = 5.4601$   $\text{\AA}$ . These values were used by Wright & Lehmann in the refinements of single-crystal data obtained at 863 K with both a synthetic and a natural quartz crystal. Other values used in the calculations are: neutron scattering lengths, for silicon and oxygen,  $0.42 \times 10^{-12}$  and  $0.58 \times 10^{-12}$  cm, respectively (Bacon, 1975); mosaic spread  $1.6 \times 10^{-3}$  rad, obtained from a rocking curve measured at 1003 K; linear absorption coefficient  $0.30 \text{ cm}^{-1}$ , determined by measuring the transmission of neutrons through amorphous silica (Mazzocchi, 1984); neutron wavelength 1.137  $\text{\AA}$ . The pattern simulations were calculated retaining terms up to the 30th order. This order was more than enough to ensure a good approximation in the intensity calculations.

To perform the structural analysis, integrated intensities were determined by means of a computer program which adjusts Gaussians to intensity data using a least-squares method in the fitting process. It is not worthwhile to give here a more detailed description of this program. It belongs to a well known class of computer programs which makes the fitting of adequate mathematical functions to curves given by points. The program lists, amongst other results, the parameters of the Gaussians adjusted to the peaks and the areas above the background of each one of the Gaussians. The program was applied to the experimental and simulated patterns and the integrated intensities of several peaks were obtained. In order to avoid large errors in the intensity integration, peaks were chosen in the experimental pattern taking into account how well a peak was isolated from its neighbors and how large was the peak-to-background ratio. It is important to note that, as mentioned before, owing to the high density of secondary reflections in the patterns, peaks resulted from the contribution of several secondary reflections with no apparent predominance of a particular one. For this reason, a peak is identified here by its azimuthal angular

position instead of a list of secondary reflections. Table 2 lists the azimuthal angular positions and integrated intensities of 14 peaks of the observed and simulated patterns. In particular, it can be observed that for both structure models the azimuthal angular positions of the peaks obtained from the simulated pattern agree within a few hundredths of a degree with those obtained from the experimental one. The agreement between observed and calculated integrated intensities was verified by calculating reliability factors according to the formula

$$R = \frac{\sum_k |I_k(\text{obs.}) - CI_k(\text{calc.})|}{\sum_k I_k(\text{obs.})}$$

where  $C$  is a scale factor relating observed [ $I_k(\text{obs.})$ ] and calculated [ $I_k(\text{calc.})$ ] integrated intensities. By varying the scale factor for a particular set of intensities, a minimum  $R$  is found, which gives the degree of agreement between patterns.

The results found for the two structure models are the following:

for the ordered model,

$$R = 0.143 \text{ with } C = 2.160 \times 10^5;$$

for the disordered model,

$$R = 0.110 \text{ with } C = 2.775 \times 10^5.$$

The above results favor Wright & Lehmann's disordered model of structure since its  $R$  factor is about 3.3% lower than that found for the ordered model adopted by Young. It is important to note that no data were refined in the intensity analysis. If any method of refinement had been employed the agreement would be better. However, the development of a method to refine parameters in a n.m.d. intensity analysis was beyond the scope of this work.

The authors express their sincere thanks to Professor S. Caticha-Ellis for many helpful discussions about the structures of  $\alpha$ - and  $\beta$ -quartz, as well as about the application of multiple diffraction to structural analysis. One of the authors, VLM, acknowledges the grant of a fellowship by the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP). This fellowship permitted her to obtain a Master of Science degree in the subject of the application of multiple diffraction to the study of the  $\alpha$  and  $\beta$  phases of quartz.

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