

Density functional calculations of polysynthetic
Brazil twinning in α -quartz

Hans Grimmer* and Bernard Delley

Research with Neutrons and Muons, Paul Scherrer Institut, CH-5234 Villigen PSI, Switzerland.

Correspondence e-mail: hans.grimmer@psi.ch

Received 19 December 2011

Accepted 27 February 2012

Polysynthetic Brazil twinning in α -quartz, which occurs commonly in amethyst, is interpreted in the literature as having its composition planes parallel to one of the faces of the major rhombohedron r . It is shown that, instead, the composition planes are parallel to one of the faces of the minor rhombohedron z . The proposed translation $0.4547a$ between neighbouring lamellae leads to binding distances and binding angles across the composition plane that differ less from their bulk values than for the translation $0.5a$ proposed in the literature. Density functional calculations show that the energy of the unrelaxed polysynthetic twin is lower for the proposed translation. They also show that relaxation increases the thickness of the polytwin by 4 pm per composition plane.

© 2012 International Union of Crystallography
Printed in Singapore – all rights reserved

1. Introduction

The stable modification of SiO_2 at ambient pressure is α -quartz (also called low quartz) for temperatures up to 846 K. α -Quartz exhibits enantiomorphism, *i.e.* its structure may be right- or left-handed. Corresponding to the sense of the rotation of polarized light propagating along the threefold axis of the crystal, α -quartz with space group $P3_121$ is called laevorotatory and α -quartz with space group $P3_221$ is called dextrorotatory.

The point group 32 of α -quartz has six elements, whereas the lattice of its symmetry translations has point group $6/mmm$ with 24 elements. It follows that four different domain states are possible for a given orientation of the translation lattice. Up to a translation, two different domains can be mapped onto each other either by a 180° rotation parallel to the threefold axis of α -quartz ($2_z \rightarrow$ Dauphiné law), by an inversion ($\bar{1} \rightarrow$ Brazil law), or by a mirror reflection perpendicular to the threefold axis ($m_z \rightarrow$ combined Dauphiné–Brazil law). Whereas the individuals related by the Dauphiné law are both either laevo- or dextrorotatory, the individuals related by the Brazil or combined law have different hands.

Also, polysynthetic Brazil twinning has been observed. Such twins consist of many parallel thin lamellae, with composition planes parallel to one of the faces of r or z . The major (or positive) rhombohedron $r\{10\bar{1}1\}$ has three faces with Bravais indices $(10\bar{1}1)$, $(0\bar{1}11)$, $(\bar{1}101)$ and three faces $(\bar{1}0\bar{1}1)$, $(01\bar{1}\bar{1})$, $(\bar{1}\bar{1}0\bar{1})$ which are parallel to the first three but have an opposite sign of the surface normal. The minor (or negative) rhombohedron $z\{01\bar{1}1\}$ has three faces with Bravais indices $(01\bar{1}1)$, $(\bar{1}\bar{1}01)$, $(\bar{1}011)$ and three faces $(0\bar{1}\bar{1}\bar{1})$, $(\bar{1}\bar{1}0\bar{1})$, $(10\bar{1}\bar{1})$ which are parallel to the first three but have an opposite sign of the surface normal.

Amethyst, the violet variety of quartz, whose colour is caused by an iron content of typically a few hundred p.p.m. by weight, almost invariably shows polysynthetic twinning on the Brazil law (Fron del, 1962).

Lu & Sunagawa (1994) investigated the textures of geode agates. These agates consist of quartz fibres. Those with a thickness larger than 50 μm usually contain polysynthetic Brazil twins, the lamellae of which have thicknesses ranging from 10 to 30 nm. In most geode agates, coarse quartz or amethyst crystals containing polysynthetic Brazil twins with a lamellae thickness of the order of 10 nm develop in the last stage. The temperature at which the agates are formed is around 323 K. The ubiquitous occurrence of Brazil twin lamellae with a thickness of nanometre scale in all quartz crystals above a certain size indicates that the embryonic particles in the hydrothermal solution had a crystal structure of low quartz with an equal proportion of left- and right-handed types (Lu & Sunagawa, 1994). Also McLaren & Phakey (1966) found that the thickness of Brazil twin lamellae can be as small as 10 nm.

Whereas it is no problem distinguishing between the r and z surfaces of a macroscopic crystal of α -quartz, the situation is different concerning the polysynthetic Brazil twins observed in amethysts. McLaren & Pitkethly (1982) stress that their transmission electron microscopy (TEM) observations do not allow them to distinguish between composition planes r and z ; similarly the traces of the composition planes intersecting the amethyst slices observed microscopically by Lu & Sunagawa (1990) may be interpreted as z instead of r . For this reason, we systematically investigated geometric models of Brazil twins with composition planes r and z and took them as starting models for density functional theory (DFT) calculations. Whereas the approximations inherent in DFT calculations lead for α -quartz to cell parameters and Wyckoff positions

Table 1

The positions $\mathbf{v} = \frac{1}{2}(\mathbf{YB} + \mathbf{ZC})$ ($0 \leq Y, Z < 1$) of the inversion $\bar{1}$, for which the superposition is monoclinic.

The space group is $C2/m$ if n is even, $C2/c$ if n is odd. Vectors **A**, **B** and **C** define a conventional C-centred monoclinic cell with monoclinic axis **B**. Its volume is $2V_0 = 3^{1/2}a^2c$, where $V_0 = \frac{1}{2}(3)^{1/2}a^2c$ is the volume of a primitive cell of quartz.

$n = 6Z$	A	B (monoclinic axis)	C
4, 1	$-\mathbf{a} - 2\mathbf{b}$	a	c
2, 5	$2\mathbf{a} + \mathbf{b}$	b	c
0, 3	$\mathbf{a} - \mathbf{b}$	$\mathbf{a} + \mathbf{b}$	c

that deviate slightly from the experimental values, such calculations show phenomena in the twin boundaries that are difficult to measure experimentally, such as relaxation of atomic positions, reduced density and increased energy compared to their bulk values.

2. The structure of α -quartz

Analysing available data, Baur (2009) proposes for α -quartz at 291 K the following parameters of the hexagonal cell: $a = 491.30$ (1), $c = 540.47$ (1) pm. Laevo-Q (short for laevorotatory quartz) has the space group $P3_121$ with Si atoms at Wyckoff position $3a$ ($t, 0, 1/3$), where $t = 0.5301$ (2), and O atoms at position $6c$ (x, y, z) with $x = 0.4139$ (5), $y = 0.1466$ (4), $z = 0.1188$ (3).

Dextro-Q (short for dextrorotatory quartz) has space group $P3_221$ with Si atoms at Wyckoff position $3a$ ($t, 0, -1/3$), where $t = -0.5301$ (2), and O atoms at position $6c$ (x, y, z) with $x = -0.4139$ (5), $y = -0.1466$ (4) and $z = -0.1188$ (3), *i.e.* the position coordinates of laevo- and dextro-Q have opposite sign (Parthé & Gelato, 1984).

These parameters lead to the following bond lengths within one coordination tetrahedron: twice each Si–O_a 160.4 pm,

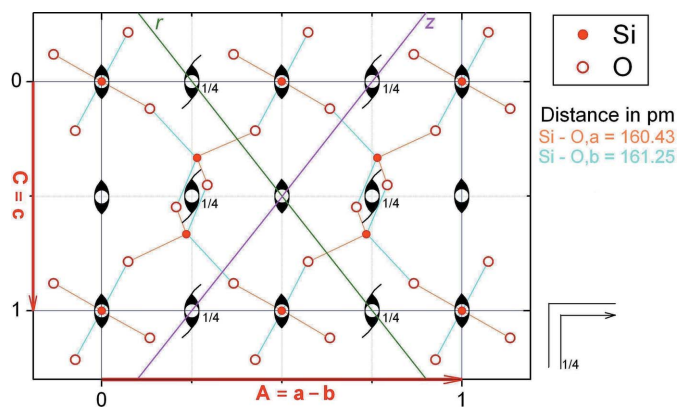


Figure 1

Projection of the superposition of a laevo-Q and a dextro-Q related by an inversion at the origin of the coordinate system. The superposition has space group $C2/m$ (No. 12); the monoclinic axis is **B** = $\mathbf{a} + \mathbf{b}$. The projections $\parallel \mathbf{B}$ of the atomic positions coincide for the laevo-Q and the dextro-Q. The letter r denotes a plane $(\bar{1}101)$ belonging to the positive rhombohedron r ; z denotes a plane (1101) belonging to the negative rhombohedron z . These planes are perpendicular to the plane of the drawing and will be considered as possible composition planes separating laevo-Q and dextro-Q.

Si–O_b 161.3 pm; the angles around the silicon atom are O_a–Si–O_a 109.0°, O_b–Si–O_b 109.5°, twice O_a–Si–O_b 110.4° and twice O_a–Si–O_b 118.8°. The Si–O–Si angle between two tetrahedra is 143.7° (Baur, 2009).

3. A model for periodic polysynthetic Brazil twins

We start by neglecting the composition plane between the two individuals, *i.e.* we first consider the superposition of the two crystals. Vector lattices being invariant under $\bar{1}$, the superposition has the same symmetry translations as the laevo-Q and the dextro-Q. It follows that its symmetry can be described by a space group. The space group of the superposition is centrosymmetric by construction. The threefold symmetry is lost because 3_1 and 3_2 have only the identity in common. The point group is therefore either $\bar{1}$ or $2/m$, depending on the choice of the position of the inversion relating the laevo-Q and the dextro-Q.

We start with the superposition for which laevo-Q and dextro-Q have their atoms at the positions given in §2, *i.e.* where the two enantiomorphs are related by $\bar{1}$ at the origin of the coordinate system. Changing the position of $\bar{1}$ by a vector \mathbf{v} corresponds to a translation $2\mathbf{v} = X'\mathbf{a} + Y'\mathbf{b} + \mathbf{Zc}$, where **a**, **b** and **c** span the conventional hexagonal cell of α -quartz. **a**, **b** and **c** being symmetry translations, it suffices to consider the range $0 \leq X', Y', Z < 1$. Consider first the special cases $2\mathbf{v} = \mathbf{Zc}$. Then the point group is $2/m$ if $Z = n/6$ (n is an integer) and $\bar{1}$ otherwise. If $Z = n/6$ then the space group is $C2/m$ if n is even, $C2/c$ if n is odd. The monoclinic axis is **a** if $n = 1$ or 4, **b** if $n = 2$ or 5, and $\mathbf{a} + \mathbf{b}$ if $n = 0$ or 3. We choose a conventional right-handed monoclinic coordinate system with basis vectors **A**, **B**, **C** = **c** with monoclinic axis **B**. Because **A**, **B** and **C** define a C-centred orthohexagonal cell (see *e.g.* Bertaut, 2002) in the case of α -quartz, we also have $\mathbf{A} \perp \mathbf{C}$, whereas the monoclinic symmetry of the superposition only requires $\mathbf{A} \perp \mathbf{B}$ and $\mathbf{C} \perp \mathbf{B}$.

Writing $2\mathbf{v} = X\mathbf{A} + \mathbf{YB} + \mathbf{ZC}$, it suffices to consider $0 \leq X < \frac{1}{2}, 0 \leq Y, Z < 1$. The type of the space group does not depend on Y , but is monoclinic only for $X = 0$. The monoclinic cases are considered in Table 1. Below we shall discuss for what values of Y the bond lengths and bond angles across the composition planes differ least from their bulk values. The models with an optimum value of Y will serve as the starting point for DFT calculations, which minimize energy by relaxing atomic positions, decreasing the density close to the composition planes and changing the parameters of the monoclinic cell.

Fig. 1 shows the situation for cell parameters $a = 491.30$, $c = 540.47$ pm and $\bar{1}$ at $\mathbf{v} = 0$. If $\mathbf{v} = \delta\mathbf{B}$ with $\delta \neq 0$, the dextro-Q will be shifted with respect to the laevo-Q by $Y = 2\delta$ along the monoclinic axis **B**. Such a shift changes in Fig. 1 only the height of the inversion points above the plane of the drawing, *e.g.* for $\delta = \frac{1}{4}$, the inversion points at heights $n/2$ (where n is an integer) and those at heights $n/2 + \frac{1}{4}$ will be exchanged because they are repeated at height differences of $\frac{1}{2}$.

We first consider polytwins with composition plane $z(\bar{1}101)$ obtained from Fig. 1 by removing in adjacent lamellae the atoms of laevo-Q or dextro-Q, respectively. Fig. 2 shows the

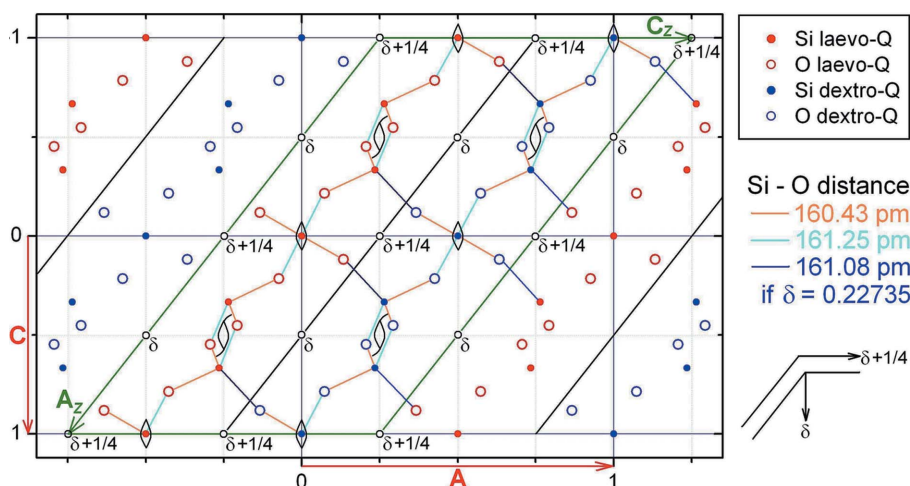


Figure 2
Threefold periodic model of the polytwin with composition plane z and minimum lamellae thickness. Centres of symmetry lie $(\delta + \frac{1}{2}n)\mathbf{B}$ or $(\delta + \frac{1}{4} + \frac{1}{2}n)\mathbf{B}$ above the plane of the drawing, n is an integer.

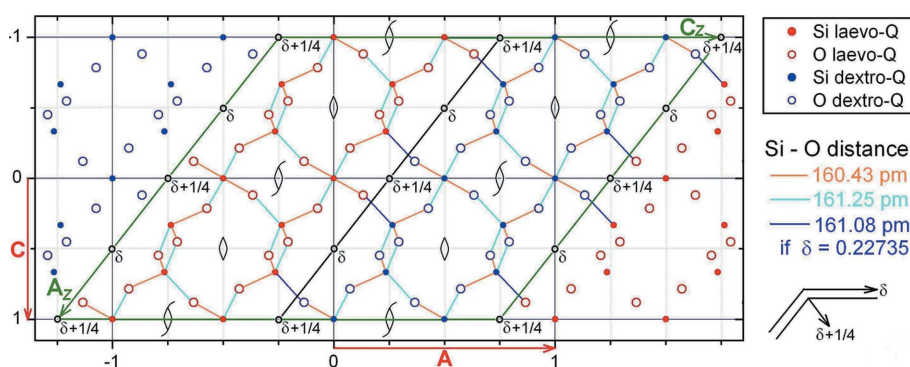


Figure 3
Threefold periodic model of the polytwin with composition plane z and twice minimum lamellae thickness. Centres of symmetry lie $(\delta + \frac{1}{2}n)\mathbf{B}$ or $(\delta + \frac{1}{4} + \frac{1}{2}n)\mathbf{B}$ above the plane of the drawing, n is an integer.

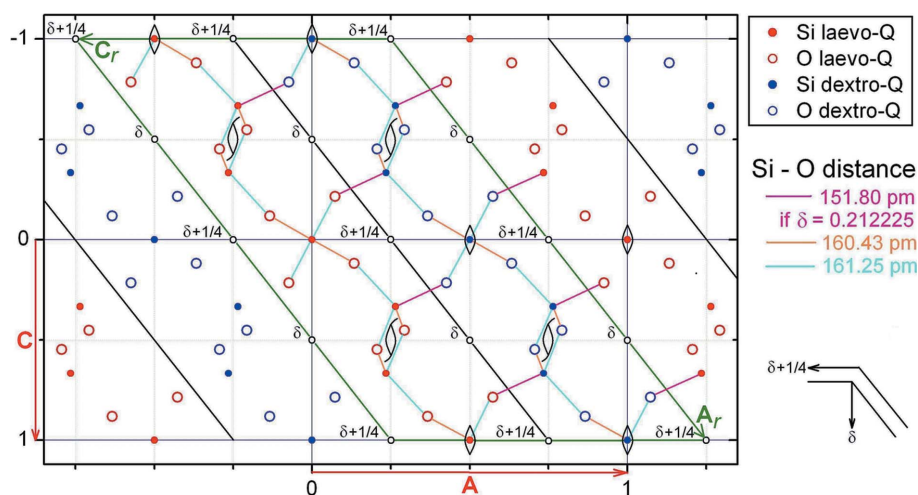


Figure 4
Threefold periodic model of the polytwin with composition plane r and minimum lamellae thickness. Centres of symmetry lie $(\delta + \frac{1}{2}n)\mathbf{B}$ or $(\delta + \frac{1}{4} + \frac{1}{2}n)\mathbf{B}$ above the plane of the drawing, n is an integer.

case with minimum thickness of the lamellae, *i.e.* each symmetry translation of quartz traverses an integer number (0, 1, 2, ...) of lamellae. The structure is threefold periodic with space group $C2/c$. Marked in green is a conventional C -centred cell of the polytwin. It is spanned by the vectors $\mathbf{A}_z = 2\mathbf{C} - \mathbf{A} = 2\mathbf{c} - \mathbf{a} + \mathbf{b}$, $\mathbf{B}_z = -\mathbf{B} = -\mathbf{a} - \mathbf{b}$ and $\mathbf{C}_z = \mathbf{A} = \mathbf{a} - \mathbf{b}$; its volume is $2V_1 = 2(3)^{1/2}a^2c$, *i.e.* four times the volume $V_0 = \frac{1}{2}(3)^{1/2}a^2c$ of a primitive cell of quartz. One factor 2 comes from the fact that the cell contains laevo- Q and dextro- Q , the other from the fact that the cell is C -centred. The ordered triple $\mathbf{A}_z, \mathbf{B}_z, \mathbf{C}_z$ defines a right-handed conventional basis with monoclinic axis \mathbf{B}_z . $\mathbf{A}_z, \mathbf{B}_z$ and $\frac{1}{2}(\mathbf{A}_z + \mathbf{B}_z) = \mathbf{c} - \mathbf{a}$ are symmetry translations that lie in the composition plane z .

Lines connecting Si and O on opposite sides of the twin boundary are marked dark blue in Fig. 2. All these lines are parallel and of equal length, not only in the projection shown in the figure but also in three-dimensional space. This is in contrast to a single crystal, where neighbouring dark-blue lines would have opposite slope in three-dimensional space. The least deviation from a single crystal is obtained for a polytwin in which the Si and O atoms connected by a dark-blue line are at the same height above the plane of Fig. 2. This is the case if $\delta = 0.22735$. The distance between neighbouring Si and O atoms on opposite sides of the twin boundary is then 161.08 pm, only 0.1% less than the 161.25 pm in the single crystal.

Fig. 3 gives the analogous results for lamellae thickness twice the minimum. Also in this case the space group is $C2/c$. Marked in green is a conventional C -centred cell of the polytwin. It is spanned by the vectors $\mathbf{A}_z = 2\mathbf{C} - \mathbf{A}$, $\mathbf{B}_z = -\mathbf{B}$ and $\mathbf{C}_z = 2\mathbf{A}$; its volume is $2V_2 = 8V_0$.

Generally, the analogous models with lamellae thickness N times the minimum, N being a positive integer, all have space group $C2/c$. The point group is therefore $2/m$, exactly as for the superposition shown in Fig. 1. The dilution of the density of symmetry elements in the polytwin models

Table 2

Comparison of the bond distances (pm) and angles ($^{\circ}$) in a single crystal with those across the composition plane z of a Brazil twin for the models proposed by McLaren & Phakey (1966) and in the present paper.

The lattice parameters and atom positions used for α -quartz are those proposed by Baur (2009). Shown also is a model with undistorted oxygen tetrahedra (model 1) and one with unchanged angles between adjacent oxygen tetrahedra (model 3).

	Single crystal	Model 1 $Y = 2\delta = 0.4395$ $\angle(\text{O}-\text{Si}-\text{O})$ unchanged	Model 2 $Y = 2\delta = 0.4547$ Grimmer– Delley	Model 3 $Y = 2\delta = 0.4699$ $\angle(\text{Si}-\text{O}-\text{Si})$ unchanged	Model 4 $Y = 2\delta = 0.5$ McLaren– Phakey
$d(\text{Si}-\text{O},\text{b})$	161.3	161.3	161.1	161.3	162.6
$d(\text{Si}-\text{O}-\text{Si})$	305.7	301.1	303.3	305.7	310.9
$d(\text{O},\text{b}-\text{Si}-\text{O},\text{b})$	263.3	263.3	260.3	257.6	252.6
$d(\text{O},\text{a}-\text{Si}-\text{O},\text{b})$	264.2	264.2	268.1	272.3	280.8
$d(\text{O},\text{b}-\text{Si}-\text{O},\text{a})$	261.5	261.5	259.9	258.5	256.4
$\angle(\text{Si}-\text{O}-\text{Si})$	143.7	138.8	141.3	143.7	148.5
$\angle(\text{O},\text{b}-\text{Si}-\text{O},\text{b})$	109.5	109.5	107.7	106.0	102.5
$\angle(\text{O},\text{a}-\text{Si}-\text{O},\text{b})$	110.4	110.4	113.0	115.6	120.7
$\angle(\text{O},\text{b}-\text{Si}-\text{O},\text{a})$	108.8	108.8	107.9	107.0	105.1

compared to the superposition is therefore given by the volume ratio of primitive cells of the polytwin and the superposition: $d = V_N/V_0 = 2N$. More precisely, the space group of the polytwin model with lamellae thickness N (*i.e.* N times the minimum value) is a subgroup of index $I = 2N$ of the space group of the superposition. Considering that the factor 2 is due to the separation of laevo- and dextro-Q, we see that $I = 2N$ is the minimum index for a periodic polytwin with lamellae thickness N .

Consider now polytwins with composition plane $r(\bar{1}101)$ obtained from Fig. 1 by removing in adjacent lamellae the atoms of laevo-Q or dextro-Q, respectively. Fig. 4 shows the case with minimum thickness of the lamellae. Again, the structure is threefold periodic with space group $C2/c$. Marked in green is a conventional C -centred cell of the polytwin. It is spanned by the vectors $\mathbf{A}_r = 2\mathbf{C} + \mathbf{A} = 2\mathbf{c} + \mathbf{a} - \mathbf{b}$, $\mathbf{B}_r = \mathbf{B} = \mathbf{a} + \mathbf{b}$ and $\mathbf{C}_r = -\mathbf{A} = -\mathbf{a} + \mathbf{b}$; its volume is $2V_1 = 2(3)^{1/2}a^2c$, *i.e.* four times the volume $V_0 = \frac{1}{2}(3)^{1/2}a^2c$ of a primitive cell of quartz. The ordered triple $\mathbf{A}_r, \mathbf{B}_r, \mathbf{C}_r$ defines a right-handed conventional basis with monoclinic axis \mathbf{B}_r . $\mathbf{A}_r, \mathbf{B}_r$ and $\frac{1}{2}(\mathbf{A}_r + \mathbf{B}_r) = \mathbf{c} + \mathbf{a}$ are symmetry translations that lie in the composition plane r .

Lines connecting Si and O on opposite sides of the twin boundary are marked red in Fig. 4. All these lines are parallel and of equal length, not only in the projection shown in the figure but also in three-dimensional space. This is in contrast to a single crystal, where neighbouring red lines would have opposite slope in three-dimensional space. The least deviation from a single crystal is obtained for a polytwin in which the Si and O atoms connected by a red line are at the same height above the plane of Fig. 4. This is the case if $\delta = 0.212225$. The distance between Si and O atoms on opposite sides of the twin boundary is then 151.80 pm, 5.4% less than the 160.43 pm in the single crystal. This deviation is 50 times larger than the corresponding value for composition plane z . Therefore, it is expected that the energy of twin boundaries with composition plane r is much higher than for composition plane z .

Among the six cases distinguished in Table 1, the one with $n = 0$ has been considered so far. The other cases with n even have the monoclinic axis of the polytwin rotated about \mathbf{C} by 120° or 240° . The cases with n odd are different: take $n = 1$. Fig. 1, which shows the situation for $n = 0$, will change as follows: the projections $\parallel \mathbf{B}$ of the atoms in dextro-Q will no longer coincide with those in laevo-Q but will be displaced by $\mathbf{C}/2$. In this case, in which the superposition has space group $C2/c$ instead of $C2/m$, no composition planes of type z or r exist that give rise to reasonable binding distances and binding angles across the composition plane.

4. Comparison with earlier work

An atomistic model of Brazil twin boundaries was proposed by McLaren & Phakey (1966). It essentially corresponds to our model for the boundary with composition plane $z(\bar{1}101)$ and $\delta = 0.25$. However, those authors claim that their model has composition plane $r(\bar{1}101)$. The reason is that they confounded the structures with space groups $P3_121$ and $P3_221$. This corresponds to using a left-handed instead of a right-handed coordinate system, *i.e.* to inverting the direction of \mathbf{c} , thus interchanging r and z .

Let us compare, for the quartz structure proposed by Baur (2009), the proposed model with $Y = 2\delta = 0.4547$ to the McLaren–Phakey model with $Y = 0.5$, and with two models in which all O–Si–O angles or the Si–O–Si angles are unchanged across the composition plane z . The O–Si–O angle unchanged means that the tetrahedra consisting of four O atoms surrounding an Si atom remain undistorted when not all O atoms lie on the same side of the composition plane; the Si–O–Si angle unchanged means that the angle between two O tetrahedra having an O atom in common remains unchanged when the Si atoms at the centres of the two tetrahedra lie on different sides of the composition plane.

Table 2 shows the bond distances and bond angles across the composition plane. Notice that all pairs Si–O,a, all triples O,a–Si–O,a and half of the triples O,a–Si–O,b and O,b–Si–O,a cannot lie on different sides of a composition plane z . In these cases, the distances d and angles \angle for all models are the same as in a single crystal, *e.g.* $d(\text{Si}-\text{O},\text{a}) = 160.4$ pm, $d(\text{O},\text{a}-\text{Si}-\text{O},\text{a}) = 261.2$ pm, $\angle(\text{O},\text{a}-\text{Si}-\text{O},\text{a}) = 109.0^{\circ}$.

Table 3 shows how much distances and angles in the various models differ from the values in a single crystal.

The values 0 in Table 3 are exactly 0; the Si–O distance across the composition plane is unchanged for models 1 and 3. For model 1 with undistorted oxygen tetrahedra all the O–Si–O angles are unchanged, with the consequence that the O–O distances in each tetrahedron also remain fixed. For model 3, with unchanged angles between adjacent tetrahedra, the Si–O–Si angle is unchanged with the consequence that

Table 3

Deviation of bond angles ($^{\circ}$) and bond distances (pm) in the various models from the values in a single crystal.

	Model 1 unchanged	Model 2 Grimmer– Delley	Model 3 $\angle(\text{Si–O–Si})$ unchanged	Model 4 McLaren– Phakey
$d(\text{Si–O},b)$	0.0	–0.2	0.0	1.4
$d(\text{Si–O–Si})$	–4.6	–2.4	0.0	5.2
$d(\text{O},b\text{–Si–O},b)$	0.0	–3.0	–5.8	–10.7
$d(\text{O},a\text{–Si–O},b)$	0.0	4.0	8.1	16.6
$d(\text{O},b\text{–Si–O},a)$	0.0	–1.6	–3.0	–5.1
$\angle(\text{Si–O–Si})$	–4.9	–2.4	0.0	4.8
$\angle(\text{O},b\text{–Si–O},b)$	0.0	–1.8	–3.5	–7.0
$\angle(\text{O},a\text{–Si–O},b)$	0.0	2.6	5.2	10.3
$\angle(\text{O},b\text{–Si–O},a)$	0.0	–0.9	–1.8	–3.7

Table 4

Total energy in eV per primitive cell: α -quartz relative to spin-unrestricted spherical atoms; β -quartz relative to α -quartz.

Columns *a* and *c* show how much the lattice parameters at which the energy becomes minimum deviate from the literature values. The following literature values were used: $a = 491.30$ pm and $c = 540.47$ pm given by Baur (2009) for α -quartz at 291 K; $a = 499.8$ pm and $c = 546.0$ pm given by Wright & Lehmann (1981) for β -quartz at 863 K.

	Functional	Basis set	Energy (eV)	<i>a</i> (%)	<i>c</i> (%)
α -Quartz	PBE	DNP	–58.407	+0.9	+1.2
	PBE	DNP_{α}	–58.363	+0.9	+1.0
	PBEsol	DNP	–61.351	–0.5	+0.1
β -Quartz	PBEsol	DNP_{α}	–61.336	–0.5	+0.0
	PBE	DNP	0.124	+2.3	+2.4
	PBE	DNP_{α}	0.127	+2.2	+2.4
	PBEsol	DNP	0.202	+1.7	+2.0
	PBEsol	DNP_{α}	0.185	+1.7	+1.9

the Si–Si distance between adjacent tetrahedra also remains fixed. Our model 2 is a compromise between 1 and 3. Because the density in the interfaces has been chosen to be the same as in the bulk for all four models, the Si–O distance across the composition plane is slightly reduced in model 2. We therefore expect that the DFT calculations will show a slight expansion perpendicular to the composition planes. The table shows that model 2 is much closer to a single crystal than model 4. We therefore expect that our model has lower energy than the one proposed by McLaren & Phakey (1966).

As mentioned in connection with Fig. 2, the Si–O bonds and the O–Si bonds across the composition plane have the same slope with respect to the plane of Fig. 2, whereas the corresponding bonds in a single crystal have opposite slope $\pm\varphi$. The slope is 0 in our model, $-\varphi$ or φ in the two models with $\angle(\text{O–Si–O})$ or $\angle(\text{Si–O–Si})$ unchanged, and $>\varphi$ for the McLaren–Phakey model.

The atomistic model of McLaren & Phakey (1966) has been referred to subsequently by Phakey (1969), by McLaren & Pitkethly (1982) and by Lu & Sunagawa (1990). McLaren & Pitkethly (1982) stress that their TEM observations do not allow them to distinguish between composition planes *r* and *z*; similarly the traces of the composition planes intersecting the amethyst slices observed microscopically by Lu & Sunagawa (1990) may be interpreted as *z* instead of *r*. This seems to be

the reason why the misinterpretation of the McLaren–Phakey model as having composition plane *r* has not been noticed earlier.

Different conventions for describing the quartz structure have been used by McLaren & Phakey (1966), Phakey (1969) and McLaren & Pitkethly (1982). Generally, many different conventions were in use before the 1980s, resulting in considerable confusion, as pointed out by Donnay & Le Page (1978). Parthé & Gelato (1984) proposed a standardization of inorganic crystal structure data, which has become a widely accepted standard. Also the recent paper of Baur (2009) makes use of this standardization, which is used in the present contribution together with his lattice and structure parameters.

5. Density functional calculations of polysynthetic Brazil twinning in α -quartz

Figs. 2 and 4 show threefold periodic models of polysynthetic Brazil twinning in α -quartz with minimum lamellae thickness compatible with the structure of α -quartz and composition plane $z(\bar{1}\bar{1}01)$ and $r(\bar{1}101)$, respectively. The lamellae thickness is 0.67 nm in both cases. Our density functional calculations start from threefold periodic models as shown in Figs. 2–4 with lamellae thicknesses being an integral multiple *N* of the minimum value of 0.67 nm, where $N = 1, 2, \dots, 6$. It has been shown in §1 that the experimentally observed width of the lamellae of polysynthetic Brazil twins may be as small as 10 nm. It follows that the threefold periodic models used as starting points of density functional calculations may not be far from reality in the case of polysynthetic twinning on the Brazil law.

The present density functional calculations use the *DMol3* code (Delley, 1990, 2000). First, the structures of α - and β -quartz have been computed for the functionals PBE as defined by Perdew *et al.* (1996) and PBEsol as defined by Perdew *et al.* (2008), using the basis sets DNP and DNP_{α} . DNP denotes a double numerical with polarization (DNP) local orbital basis set (Delley, 1990); DNP_{α} is a DNP basis set optimized to minimize total energy for the experimental α -quartz structure (Delley & Grimmer, 2007). The cutoff radii used for the basis functions were $6.88 a_0$ for O and $10.06 a_0$ for Si, where a_0 denotes the Bohr radius. The calculations minimized energy with respect to the parameters defining the cell and the Wyckoff positions, starting out with the values given by Baur (2009) for α -quartz at 291 K and by Wright & Lehmann (1981) for β -quartz at 863 K. The results are given in Table 4. Note that the PBE and PBEsol energy minima are lower for DNP than for DNP_{α} .

In contrast to Delley & Grimmer (2007), where the functional PBE has been used together with the basis set DNP_{α} , the functional PBEsol will be used together with the original basis set DNP for the present calculations. Whereas PBE has a tendency of overestimating the cell volume (it gave for *a* a value 0.8% higher than 491.0 pm and for *c* a value 1% higher than 540.2 pm), PBEsol underestimates the cell volume of α -quartz, giving $a = 488.82$ pm and $c = 540.86$ pm, the former

Table 5

Cell parameters (pm) and Wyckoff parameters, bond distances (pm) and angles (°) obtained for α -quartz by DFT calculations with functional PBEsol and basis set DNP.

Comparison with the experimental values of Lager *et al.* (1982) at 13 K and of Baur (2009) at 291 K.

		DFT at 0 K	Lager <i>et al.</i> at 13 K	Baur at 291 K	
Cell parameters	<i>a</i>	488.82	490.21	491.30	
	<i>c</i>	540.86	539.97	540.47	
Wyckoff parameters	Si	<i>t</i>	0.5364	0.5320	0.5301
	O	<i>x</i>	0.4084	0.4124	0.4139
		<i>y</i>	0.1291	0.1412	0.1466
		<i>z</i>	0.1083	0.1163	0.1188
Distances	Si—O,a	162.77	161.20	160.43	
	Si—O,b	163.24	161.31	161.25	
	Si—O—Si	305.27	305.30	305.71	
	O,a—Si—O,a	263.97	262.29	261.21	
	O,b—Si—O,b	266.82	263.27	263.32	
	O,a—Si—O,b	269.08	265.33	264.18	
	O,b—Si—O,a	264.07	261.85	261.51	
Angles	Si—O—Si	138.90	142.41	143.73	
	O,a—Si—O,a	108.36	108.89	108.99	
	O,b—Si—O,b	109.62	109.38	109.47	
	O,a—Si—O,b	111.25	110.71	110.42	
	O,b—Si—O,a	108.19	108.57	108.77	

being 0.50% less and the latter 0.07% more than the values $a = 491.30$ pm and $c = 540.47$ pm proposed by Baur (2009). PBEsol obtains the energy minimum -61.351 eV for α -quartz at the following Wyckoff position parameters: $t = 0.5364$ for Si and $x = 0.4084$, $y = 0.1291$, $z = 0.1083$ for O.

For β -quartz the deviations are larger, the reason being that the DFT calculations are based on the assumption that the structure of β -quartz is reached by a displacive phase transition. However, the neutron diffraction results of Wright & Lehmann (1981) indicate that the structure of β -quartz is reached by an order-disorder transition, in which a Dauphiné twin structure of α -quartz becomes correlated over short distances at the transition temperature, giving an average structure with higher symmetry.

The DFT calculation corresponds to α -quartz at 0 K. Therefore, we shall compare its results in Table 5 not only with the experimental values of Baur (2009) at 291 K (close to the temperature at which geode agates were formed) but also to those of Lager *et al.* (1982) at 13 K.

Table 5 shows that the values obtained from DFT calculations lie, as expected, closer to those of Lager than those of Baur with only three exceptions: c , the angle (O,b—Si—O,b) and the distance between these two oxygen atoms.

The cell parameters given in Table 5 lead to the following values of the monoclinic angle of the conventional C -centred monoclinic cell for the z - and r -type polytwins considered in §3: $\beta = 128.21^\circ$ for the parameters of Baur, $\beta = 128.17^\circ$ for the parameters of Lager and $\beta = 128.05^\circ$ for the DFT parameters.

The DFT calculations confirmed our expectation that the model proposed in this paper has lower energy than the one

Table 6

Energies and displacements of Brazil polytwins with composition plane z .

The lamellae thickness is given as a multiple N of the minimum value compatible with the structure of quartz. E_{twin} is the energy difference between polytwin and single crystal per primitive cell of the polytwin, which contains a pair of interfaces. Stretch gives the extension of the monoclinic cell normal to the interface, shear parallel to the interface and normal to the monoclinic axis. β is the obtuse angle of the conventional C -centred monoclinic cell. A cell with least obtuse angle was chosen for minimum lamellae thickness; cells with similar values of β were chosen for thicker lamellae.

Lamellae thickness N	E_{twin} (eV)	Stretch (pm)	Shear (pm)	β (°)
1	0.0371	2.2	-16.8	128.86
2	0.0537	7.8	-16.3	128.33
3	0.0564	7.5	-17.2	128.26
4	0.0550	7.9	-17.1	128.21
5	0.0552	7.6	-16.9	128.18
6	0.0545	7.6	-16.9	128.16

proposed by McLaren & Phakey (1966): whereas the energy per primitive unit cell of a polytwin with minimum lamellae thickness is 0.087 eV larger for our model than for a single crystal, it is 0.350 eV larger for the model of McLaren & Phakey (1966). The corresponding values for double lamellae thickness are 0.088 eV and 0.363 eV.

In the second step of the DFT polytwin calculations, atom positions were varied to minimize energy, keeping the lattice parameters constant. This step led to almost identical results for the two starting models: compared to a single crystal, the energy per primitive cell of the polytwin was 0.055 eV higher for minimum lamellae thickness and 0.064 eV higher for double thickness. This shows that relaxation of the atomic positions reduces the energy per primitive cell of the polytwin with double lamellae thickness by 0.299 eV with respect to the McLaren-Phakey model and by 0.024 eV with respect to our model.

The DFT calculations of the polytwin used a primitive cell spanned by $\frac{1}{2}(\mathbf{A}_z + \mathbf{B}_z) = \mathbf{c} - \mathbf{a}$, $\mathbf{B}_z = -\mathbf{a} - \mathbf{b}$ and $\mathbf{C}_z = N(\mathbf{a} - \mathbf{b})$. The first two vectors, which are parallel to the composition planes, were kept fixed in the third step of the DFT calculations, whereas the components of \mathbf{C}_z perpendicular to \mathbf{B}_z were varied to minimize energy. (Notice that a component of \mathbf{C}_z parallel to \mathbf{B}_z would destroy the monoclinic symmetry.) Energy minimization led to a stretch of the cell perpendicular to the composition planes, and to a shear parallel to these planes and perpendicular to the monoclinic axis. The shape of the monoclinic cell and the energy of polytwins of various lamellae thickness are compared in Table 6 with the corresponding values for a single crystal.

The table states that the polytwin structure is stretched perpendicularly to the composition planes. This was expected because the density is generally lower in interfaces than in the bulk. Stretch and interface energy are smallest for minimum lamellae thickness. This may be interpreted as follows: the polytwin with minimum lamellae thickness may be considered as a monoclinic phase of SiO_2 with energy only slightly higher than the energy of α -quartz. The polytwins with thicker lamellae then have alternate layers of monoclinic SiO_2 and of α -quartz.

Table 7

Energies and displacements of Brazil polytwins with composition plane r .

The lamellae thickness is given as a multiple N of the minimum value compatible with the structure of quartz. E_{twin} is the energy difference between polytwin and single crystal per primitive cell of the polytwin. Stretch gives the extension of the monoclinic cell normal to the interface, shear parallel to the interface and normal to the monoclinic axis.

Lamellae thickness N	E_{twin} (eV)	Stretch (pm)	Shear (pm)
1	0.436	37.9	37.7
2	0.520	36.1	34.7
3	0.526	36.7	33.7
4	0.522	36.2	34.6
5	0.526	35.9	33.3
6	0.523	36.0	33.4

Twinning also produces a shear of ~ -17 pm, independent of lamellae thickness. This shear leads to an increase of the obtuse angle β of the conventional C -centred monoclinic cell compared to its value of 128.05° in a single crystal; the increase of β is smaller the larger the distance between neighbouring composition planes.

Results analogous to those presented in Table 6 for Brazil twins with composition plane z are given in Table 7 for composition plane r . The interface energies are approximately ten times higher, the stretches five times larger and the absolute values of the shears doubled.

6. Summary

It has been shown that the model of a Brazil twin boundary given by McLaren & Phakey (1966) has its composition plane parallel to a face of the minor rhombohedron z , not to a face of the major rhombohedron r . A translation between neighbouring lamellae has been proposed that leads to bond distances and bond angles across the composition plane that differ two to four times less from their bulk values than for the translation proposed by McLaren & Phakey (1966). The existence of a composition plane for Brazil twins that leads to bond distances and angles that deviate very little from their bulk values helps to explain why Brazil polytwins with

composition plane z and very fine lamellae thickness are formed when low quartz is precipitated from hydrothermal solutions.

Density functional calculations show that our unrelaxed model has four times lower energy than the previous model. They also show that relaxing the models with lamellae thickness N times the minimum value of 0.67 nm gives for $N \geq 2$ almost constant values of the interface energy and of the deformation of the monoclinic unit cell of the polytwin perpendicular and parallel to the composition planes. A Brazil twin with composition plane parallel to r would have approximately ten times higher interface energy and would be stretched about five times more perpendicular to the interface and sheared about twice as much parallel to the interface.

References

- Baur, W. H. (2009). *Z. Kristallogr.* **224**, 580–592.
- Bertaut, E. F. (2002). *International Tables for Crystallography*, Vol. A, edited by Th. Hahn, pp. 62–75. Dordrecht: Kluwer Academic Publishers.
- Delley, B. (1990). *J. Chem. Phys.* **92**, 508–517.
- Delley, B. (2000). *J. Chem. Phys.* **113**, 7756–7764.
- Delley, B. & Grimmer, H. (2007). *Phys. Rev. B*, **76**, 224106.
- Donnay, J. D. H. & Le Page, Y. (1978). *Acta Cryst.* **A34**, 584–594.
- Frondel, C. (1962). *The System of Mineralogy*, Vol. III. New York: Wiley.
- Lager, G. A., Jorgensen, J. D. & Rotella, F. J. (1982). *J. Appl. Phys.* **53**, 6751–6756.
- Lu, T. J. & Sunagawa, I. (1990). *Phys. Chem. Mineral.* **17**, 207–211.
- Lu, T. J. & Sunagawa, I. (1994). *Mineral. J.* **17**, 53–76.
- McLaren, A. C. & Phakey, P. P. (1966). *Phys. Status Solidi*, **13**, 413–422.
- McLaren, A. C. & Pitkethly, D. R. (1982). *Phys. Chem. Mineral.* **8**, 128–135.
- Parthé, E. & Gelato, L. M. (1984). *Acta Cryst.* **A40**, 169–183.
- Perdew, J. P., Burke, K. & Ernzerhof, M. (1996). *Phys. Rev. Lett.* **77**, 3865–3868.
- Perdew, J. P., Ruzsinszky, A., Csonka, G. I., Vydrov, O. A., Scuseria, G. E., Constantin, L. A., Zhou, X. & Burke, K. (2008). *Phys. Rev. Lett.* **100**, 136406.
- Phakey, P. P. (1969). *Phys. Status Solidi*, **34**, 105–119.
- Wright, A. F. & Lehmann, M. S. (1981). *J. Solid State Chem.* **36**, 371–380.