GROWTH TWINNING STABILITY OF QUARTZ CROSSES
AND GENERAL GEOBAROTHERMOMETRIC IMPLICATIONS

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0. Introduction.

In dealing with growth twinning, it is interesting to analyze whether the morphology exhibited by the composite body allows the crystalline formation to always be in the most favorable circumstances for growth, no matter how the growth-site conditions can change. In fact, observations indicate that growth twinning usually originates at the beginning of the crystallization, and persists throughout the whole growth process, which is in turn influenced by the external temperature and pressure variations.

Now, a common point of view assumes that these most favorable conditions be those allowing for stable stress-free equilibrium configurations (natural states) of the (poly-)crystalline edifices.

Hence, a growth twin which is not a fortuitous, randomly generated association, is most likely to exhibit a structure which is capable of adjusting to the environmental changes taking place during the crystallization, in such a way that:

a) the polycrystal remains in the best conditions for a continuous growth
process, independently of the growth-site evolution;
b) interfacial energies are kept low and stress is not created at the
joints, so that fracture is less likely to occur.
Such formations will feature in this way all the main characteristics
attributed to genuine twins, including "reproducibility" (see FRIEDEL [1],
CAHN [2]), and very low boundary energies (see CAHN [2, pages 392-3],
BUERGER [3, p. 470-1, 475], HOLSER [4]).
Having this in mind, and adopting the viewpoint of non-linear thermo-
elasticity theory, we study here in detail the possible natural states of a
particular cross-shaped cyclic twin in quartz, as a function of two envi-
ronmental parameters, $p$ and $\theta$. By means of these variables, in fact, a
reasonably accurate description of most growth sites is obtained: $p$
expresses the intensity of the external hydrostatic load on the crystal
while growing in contact with a heat bath of temperature $\theta$.
The respective domains $I$ and $J$ of $p$ and $\theta$ are restricted enough so as to
keep the body away from phase transitions. It is also supposed that $I$ and $J$
contain the atmospheric pressure and room temperature values $p_0$ and $\theta_0$,
respectively.
It turns out that the twinning law is sensitive to the environmental
conditions, and that the twins above can experience such natural states if
and only if the values of $p$ and $\theta$ identically satisfy an equation of the form
$f(p, \theta) = 0$, where $f$ is a function that only depends on the physical
properties of the crystal considered.
An important outcome of this result is that interesting information about
the growth-site parameters $p$ and $\theta$ is obtained in this way, allowing us to
trace the past history of the material.
REMARK I: The same procedures adopted can in principle be applied to asso-
ciations other than the ones treated here. This is a new mineralogic
technique of quantitative geobarothermometry, based on the analysis of the
morphology of twinned crystals.
REMARK II: Formation of crosses by intergrowth of homogeneous congruent
individuals is rare in quartz: it is much more common in other minerals, for
instance staurolite. Nevertheless, quartz was chosen because its physical
properties are rather well known: an explicit assessment of the form of the
function $f = f(p, \theta)$ and the barothermometric path $f(p, \theta) = 0$ will be calcu-
lated using the available data.
1. Preliminaries and structural data.

Low-quartz crystallizes in the trigonal trapezohedral class of the rombohedral subsystem. The lattice type is hexagonal (see DANA [5, vol. 3]). This implies that a homogeneous configuration for a quartz crystal can be described by means of a number of interpenetrating hexagonal Bravais lattices, the position of each atom being given by (here and in the sequel, the summation convention will be understood):

\[ x = M^i E_{a^i} + p_k, \quad i=1, 2, 3, \quad M^i \text{ integers}, \]

in terms of appropriate lattice vectors \( E_a \) and "shift" vectors \( p_k, k \) ranging from zero to a suitable integer \( N \), see JAMES [6], PITIÉ [7]. Nevertheless, a common, less precise model is widely used, in which crystal configurations are described by means of one "fundamental" Bravais lattice generated by the three lattice vectors \( E_a \) only. In a sense, this corresponds to ignoring the crystal microstructure, in that lattice points are considered to represent clusters of atoms (Si and O atoms for quartz) rather than one atom alone. The adoption of this practice will not affect our results, even though it leads to a less detailed description that, for instance, fails to identify, in quartz, Dauphiné' twinned configurations. Clearly, this greatly simplifies the description of atomic movements, not allowing for instance for phenomena known as shuffling, i.e. for movements of atoms about the lattice points, which are not of interest here.

As usual, lattice vectors \( E_a \) for quartz are chosen such that:

\[ C_{ab} = E_a \cdot E_b = \begin{bmatrix} a_0^2 & -\frac{1}{2} a_0^2 & 0 \\ -\frac{1}{2} a_0^2 & a_0^2 & 0 \\ 0 & 0 & c_0^2 \end{bmatrix}, \]

where \( a_0 \) and \( c_0 \) are the lattice parameters of the hexagonal cell at room temperature and atmospheric pressure. Their values are given by several authors (see for instance LEVIEN et al. [8], JORGENSEN [9], LE PAGE and DONNAY [10]), and in DANA [5, vol. 3, p. 21] they are as follows:

\[ a_0 = 4.90290 \, \text{Å}, \quad c_0 = 5.39365 \, \text{Å}, \quad \text{whence} \quad \frac{c_0}{a_0} = 1.100. \]
The dual vectors $E^a$ ("reciprocal lattice vectors") are introduced as usual through the relations $E_a E^b = \delta_a^b$, so that we get:

\begin{equation}
(1.4) \quad E_a = C_{ab} E^b, \quad E^b = C^{ba} E_a, \quad C^{ba} C_{ac} = \delta_c^b.
\end{equation}

Explicitly:

\begin{equation}
(1.5) \quad E^1 = (1/a_0^2)[(4/3)E_1 + (2/3)E_2], \quad E^2 = (1/a_0^2)[(2/3)E_1 + (4/3)E_2],
\end{equation}

\begin{equation}
E^3 = (1/c_0^2)E_3.
\end{equation}

Lattice points are then given by

\begin{equation}
(1.6) \quad X_n = M_n^a E_a,
\end{equation}

where the $M_n^a$ are sets of integers, any such set giving the position of a "motif" of Si-O atoms.

Now, let us consider the group containing all the orthogonal transformations $Q$ satisfying the equations

\begin{equation}
(1.7) \quad QE_a = h_a^b E_b,
\end{equation}

with the matrix $h_a^b$ belonging to $GL(3, \mathbb{Z})$, the group of three dimensional unimodular matrices with integral entries. The group of $Q$'s defined by (1.7) is called the point group of the lattice generated by the vectors $E_a$, and the related group of $h$'s is the "lattice group", according to \textsc{ericksen} [11]. The latter depends on the lattice vectors $E_a$, and both groups describe the geometrical symmetry of the configuration generated by $E_a$.

In the present case, it is readily shown that conditions (1.2) and (1.7) deliver the full hexagonal holohedral group, whose corresponding lattice group is generated for instance by the three following elements

\begin{equation}
(1.8) \quad \tau = \begin{bmatrix} 1 & 0 & 0 \\ -1 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad C = \begin{bmatrix} 1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{and} \quad 1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}.
\end{equation}
for which the relations

\[ \tau^2 = 1, \quad \mathcal{C}^6 = 1, \quad \mathcal{I}^2 = 1, \quad \tau \mathcal{C} = \mathcal{C}^{-1} \tau, \quad \mathcal{I} \mathcal{C} = \mathcal{C} \quad \mathcal{I} \tau = \tau \mathcal{I} \]

hold.

However, the fact that quartz is a multi-lattice rather than a 1-lattice as discussed above, reduces its actual group of symmetries to the following subgroup of the hexagonal group, as is made clear for instance by Vigoreux and Booth [12]:

\[ (1.9) \]

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix},
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix},
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix},
\begin{bmatrix}
-1 & -1 & 0 \\
-1 & -1 & 0 \\
0 & 0 & 1
\end{bmatrix},
\begin{bmatrix}
0 & 1 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1
\end{bmatrix}
\]

This happens because some of the symmetry operations in (1.10), while leaving the fundamental lattice invariant, do not restore the motif. For instance, take the operation

\[
\begin{bmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix},
\]

which corresponds to a rotation of \( \pi \) about \( \mathbf{E}_3 \), and which belongs to (1.8) but not to (1.9): it is the operation that, in a Dauphiné twin, brings the parent configuration of the crystal to the twinned one, characterized by a different disposition of atoms about points of the same fundamental lattice as the parent phase. The point group (1.9) is called trigonal trapezohedral and gives the name to quartz's crystallographic class; it features one "optical" axis of threefold symmetry and three "polar" twofold axes of symmetry perpendicular thereto and separated by angles of 120°. The lattice vector \( \mathbf{E}_3 \) chosen above lies along the optical axis, whereas \( \mathbf{E}_1 \) and \( \mathbf{E}_2 \) lie along two of the polar axes.

2. Ch. Friedel's twinning law.

Quartz is known to twin according to a number of laws, which are described for instance in the treatise DANA [5, vol. 3, pages 97–98]. One of these laws, the one named after Ch. Friedel, is not very common, but
it is interesting and worth a closer study. It has been reported as occurring in artificial quartz by CURIÉN and KERN [13] and CURIÉN [14], and in natural quartz crystals by FRIEDLÄNDER [15], where cross-shaped formations, among others, are described [15, fig. 4].

The exact twinning law has not been given a definite and unique interpretation, according to [5]; nevertheless, it is described as follows in [13, p. 123] and [14]: "les deux individus sont tournés par rapport l'un à l'autre de 90° exactement, autour de la direction [1 1 0]." The two individuals are rotated one another through a right angle, the rotation axis being rational with indices [1, -1, 0, 0] in the four-index notation commonly used for hexagonal lattices (1). The interface (contact plane) is not indicated.

We will rely on the above description, and will thus assume that, at room temperature and atmospheric pressure, the lattice vectors $R_0E_a$ for the twinned configuration are given in terms of the parent lattice vectors $E_a$, introduced through equation (1:2), by means of a rotation $R_0$ as follows:

$$
R_0E_a = R_0^d E_d \quad \text{with} \quad R_0^d = \begin{bmatrix}
\frac{1}{2} & -\frac{1}{2} \\
-\frac{1}{2} & \frac{1}{2} \\
-c_0/a_0 & -c_0/a_0
\end{bmatrix}
\begin{bmatrix}
\frac{1}{2} a_0/c_0 \\
\frac{1}{2} a_0/c_0 \\
0
\end{bmatrix}
$$

$R_0$ is obviously not in $G$, and it is called the twinning operation. Its period is 4, and its axis, given by $E_2-E_1$, lies on the basal $<E_1, E_2>$ plane:

$$
R_0^4 = 1, \quad R_0(E_2-E_1) = E_2-E_1.
$$

Let us consider the net $\mathcal{M}$ of lattice points belonging to the crystallographic plane (2) in the parent lattice whose normal direction is given by the vector $M_0 = -E^1-E^2-2(c_0/a_0)E^3$, and let us consider the image $R_0 \mathcal{M}$ of $\mathcal{M}$ under $R_0$: $R_0 \mathcal{M}$ is a net of the twinned lattice belonging to the plane $\mathcal{M}$, say, whose normal, not of unit length, is

$$
N_0 = R_0M_0 = E^1+E^2-2(c_0/a_0)E^3 = (2/a_0)(E_1+E_2-(a_0/c_0)E_3).
$$

It is easy to see that $R_0 \mathcal{M}$ is also a net of the parent lattice: this can be checked directly on the lattice points of $R_0 \mathcal{M}$, which satisfy equation (1:6).
Thus \( \mathcal{A}_0 \) is a crystallographic plane for both the parent and the twinned lattices, upon which they both share a net of points. For this reason \( \mathcal{A}_0 \) will be assumed as the interface at which the two individuals of a Ch. Friedel's twin meet. Since the angle \( \mathcal{A}_0 \) forms with the basal \( \langle E_1, E_2 \rangle \) plane is \( \pi/4 \), the assumption above is supported by the observations reported by FRIEDLAENDER [15, figs. 3 and 4].


Insofar, crystalline configurations have been introduced through the "molecular" description given in terms of lattice vectors, but we intend here to model the crystal behaviour by means of non linear thermoelasticity theory (see for instance COLEMAN and NOLL [16], or TRUESDELL [17], but see also ERICKSEN [11], [18]-[24], PITTERI [7], [25]-[27], JAMES [6], [28], [29] for recent work on crystal elasticity).

The macroscopic viewpoint adopted here will be connected to the molecular description via the Cauchy-Born hypothesis (see ERICKSEN [19]), that we will briefly illustrate below in sect. 6.

Let us choose any reference configuration \( R \) for the crystalline body. Following TRUESDELL [17], we suppose \( R \) is the closure of an open set. Moreover, given its physical meaning, we also suppose it is a bounded regular domain. Its macroscopic deformation is given by an invertible function \( \chi: R \rightarrow \mathbb{R}^3 \), mapping \( R \) onto the present shape \( \chi(R) \subset \mathbb{R}^3 \) and giving the present position \( \mathbf{x} = \chi(\mathbf{X}) \) of the typical (material) point \( \mathbf{X} \) of \( R \).

It will be assumed that \( \chi \) is continuous and piecewise differentiable and that its gradient \( \mathbf{F}(\mathbf{X}) = \mathbf{D}\chi(\mathbf{X}) \) satisfies the condition

\[
(3.1) \quad j = \det \mathbf{F} > 0.
\]

Denoting as usual by \( \mathbf{A}^t \) the transpose of a tensor \( \mathbf{A} \), the polar decomposition of the deformation gradient \( \mathbf{F} \) reads \( \mathbf{F} = \mathbf{R}\mathbf{U} \), where \( \mathbf{R} \) is a rotation \( (\mathbf{R}\mathbf{R}^t = 1, \det \mathbf{R} = 1) \), and \( \mathbf{U} = (\mathbf{F}^t\mathbf{F})^{1/2} \) is the symmetric, positive-definite "stretch" tensor; the right Cauchy-Green tensor is then defined by:

\[
(3.2) \quad \mathbf{C} = \mathbf{F}^t\mathbf{F} = \mathbf{U}^2.
\]
In thermoelasticity theory, the material response of the elastic crystal is supposed to be fully accounted for by giving a smooth constitutive function which specifies the internal energy per unit reference volume in terms of the deformation gradient $D\chi(\chi)$ and of the entropy density field $\eta(\chi)$. We assume that the body is made of homogeneous material, this meaning that a reference configuration $R$ can be picked so that the constitutive equations are the same for all body points. Hence:

\begin{equation}
\varepsilon = \varepsilon(F, \eta)
\end{equation}

for all $\eta$ in a suitable interval and all $F$ in $D = \{ F : \det F > 0 \}$. Furthermore, we assume $\varepsilon$ is Galilean invariant:

\begin{equation}
\varepsilon(F, \eta) = \varepsilon(QF, \eta)
\end{equation}

holds for all rotations $Q$, all $F$ in the domain $D$ and all $\eta$. This means that an arbitrary rigid rotation of the final deformed configuration does not affect the value of the internal energy. The above restriction implies:

\begin{equation}
\varepsilon(F, \eta) = \varepsilon(U, \eta) = \varepsilon(C, \eta),
\end{equation}

where $U$ and $C$ are the tensors introduced in (3.2). When the reference configuration $R$ is undistorted (such is for instance the one generated by the lattice vectors $E_a$ introduced in sect.1), the classical point of view about material symmetry in crystal elasticity presumes that the form of $\varepsilon$ will reflect the geometrical symmetry of $R$, in the sense that the condition

\begin{equation}
\varepsilon(F, \eta) = \varepsilon(FR, \eta),
\end{equation}

is to hold for all $F$, $\eta$ and for all rotations in the point group described by (1.9). From (3.5-6) we immediately get:

\begin{equation}
\varepsilon(C, \eta) = \varepsilon(R^tCR, \eta),
\end{equation}

an invariance property satisfied for any symmetric, positive-definite tensor $C$ and any $R$ in the point group.

Let a new reference configuration $R'$ be picked, which is rigidly rotated
with respect to $R$, and let us call $R_0$ the rotation such that $R_0R = R'$. The response function $\varepsilon'(F, \eta)$ relative to the new configuration $R'$ is then defined by the first of the following relations (see Truesdell [17, p. 163]):

\begin{equation}
(3.8) \quad \varepsilon'(F, \eta) = \varepsilon(\text{FR}_0, \eta), \quad \text{so that} \quad \varepsilon'(C, \eta) = \varepsilon(\text{R}_0^t \text{CR}_0, \eta).
\end{equation}

When $R_0$ is not in the point group of the crystal, by (3.7-8) we have $\varepsilon(C, \eta) = \varepsilon'(C, \eta)$, so that $R$ and $R'$ are not peer, in the jargon of [17]. Finally, we define the Piola-Kirchhoff stress tensor $S = \varepsilon_F$ and the Cauchy stress tensor $T = \varepsilon_T - \varepsilon_F F^T$.

4. **Natural states for homogeneous quartz crystals and Ch. Friedel's twins**

According to the viewpoint adopted in the Introduction, we are now interested in investigating the possible existence of surfaces or paths (i.e. two- or one-parameter families) of natural states of low-quartz polycrystals grown according to Ch. Friedel's twinning law (2.1). To this end, let us begin by describing the homogeneous natural states for a quartz crystal, whose reference configuration $R$ is picked now, once and for all, as the one generated by the lattice vectors $E_a$ of low quartz at room temperature and atmospheric pressure, see (1.2-3).

In this context, a surface of stable equilibria for the crystal is meant as a family of homogeneous deformations $x = \mathbf{X}(x, p, \theta) = \overline{\mathbf{F}}(p, \theta) x'$, $\overline{\mathbf{F}} \in D$, and entropy density values $\eta = \overline{\eta}(p, \theta)$, that, for fixed values of the environmental parameters $p$ and $\theta$, minimize the total ballistic free energy functional of the body

$$ P[x, \eta, p, \theta] = \int_R \tilde{\Pi}[C(x), \eta(x), p, \theta] dX, $$

(see Ericksen [24], Coleman [30], James [28]).

Here, $C(x) = Dx^t(x)Dx(x)$, and

\begin{equation}
(4.1) \quad \pi = \tilde{\Pi}(C, \eta, p, \theta) = \varepsilon(C, \eta) - \theta \eta + p j
\end{equation}
is the ballistic free energy per unit reference volume. The minimizing condition requires that $\bar{x}$ and $\bar{\eta}$ satisfy

\begin{equation}
\int_R \hat{F}(C(x),\eta(x),p,\theta) \, dx \geq \int_R \hat{F}(\bar{C}(p,\theta),\bar{\eta}(p,\theta),p,\theta) \, dx
\end{equation}

(here $\bar{C}(p,\theta) = \bar{F}^t(p,\theta)\bar{F}(p,\theta)$) for all continuous piecewise differentiable deformations $x = \chi(x)$ in a suitable neighborhood $N_{\bar{x}}$ of $\bar{x}$ to be specified below, for all continuous piecewise differentiable entropy density functions $\eta = \eta(x)$, and for arbitrary, fixed values of $p$ and $\theta$ in $I$ and $J$ respectively.

From (3.8) and (4.1) we see that $\hat{F}$ exhibits the same symmetries as $\hat{E}$, this meaning that the relation

\begin{equation}
\hat{F}(C,\eta,p,\theta) = \hat{F}(R^tCR,\eta,p,\theta)
\end{equation}

holds for all symmetric, positive-definite $C$, all rotations $R$ in the point group and all admitted values of $\eta$, $p$, $\theta$.

Now, the homogeneous deformations $\bar{x}(x,p,\theta)$ and the entropy values $\bar{\eta}(p,\theta)$ satisfy (4.2) if and only if the pair $\bar{C}(p,\theta)$ and $\bar{\eta}(p,\theta)$ minimizes the integrand for fixed $p$ and $\theta$, i.e. if and only if

\begin{equation}
\hat{F}(\bar{C}(p,\theta),\bar{\eta}(p,\theta),p,\theta) \leq \hat{F}(C,\eta,p,\theta)
\end{equation}

holds for all $\eta$ and all $C$ in a neighborhood $N_{\bar{C}}$ of $\bar{C}(p,\theta)$. Here, $x \in N_{\bar{x}}$ if and only if $DX^tDX \in N_{\bar{C}}$ for all $X \in R$, so that $\bar{x}$ is a weak relative minimizer, according to James [29].

When $\hat{F}$ is continuously differentiable, we get from (5.4):

\begin{equation}
\hat{F}_C = 0, \quad \hat{F}_\eta = 0,
\end{equation}

where the derivatives are evaluated at $C = \bar{C}$ and $\eta = \bar{\eta}$. (4.5) and (4.1) yield, at $C = \bar{C}$ and $\eta = \bar{\eta}$:

\begin{equation}
\hat{E}_\eta = \theta,
\end{equation}

and since $\hat{E}_\eta$ is the absolute temperature of the body, we see that the envi-
ronmental and body temperatures are the same at equilibrium. The part \( \varepsilon - \theta \eta \) of the ballistic free energy \( \pi \) thus coincides with the Helmoltz free energy \( \phi \), which is usually given in a natural way as a constitutive function of \( C \) and \( \theta \). Therefore, in agreement with James [28, eqs. (4.28-29)]:

\[
\pi = \hat{\phi}(C, p, \theta) = \phi(C, \theta) + p \mathbf{j},
\]

and we will consider this equation instead of (4.1). Notice that \( \hat{\phi} \) obviously enjoys the same invariance properties (4.3) as \( \phi \).

As a consequence of (4.5), it is easily seen that the Cauchy stress \( T \) in the crystal reduces to an uniform pressure: \( T = -p \mathbf{j} \).

It is well known that the heat capacity (or specific heat) at constant configuration of a thermoelastic material is related to the second entropy derivatives of the specific internal energy function \( \varepsilon(C, \eta) \) in such a way that they both have the same sign. Now, away from phase transitions, the specific heat is expected to be a positive function, and we accordingly assume, as usual, that \( \varepsilon_{\eta \eta} > 0 \). Therefore, the minimization (4.4) can be carried out separately in the two variables \( C \) and \( \eta \), and once the minimum in \( \eta \) is determined (whose value is not of interest here), the problem (4.4) for \( \hat{\phi} \) turns out to be equivalent to the following for \( \hat{\phi} \):

\[
\hat{\phi}(C(p, \theta), p, \theta) \leq \hat{\phi}(C, p, \theta),
\]

to hold for all symmetric, positive-definite \( C \in \mathbb{S} \) and all fixed \( p, \theta \).

Condition (4.8) granted, the tensor \( \overline{C}(p, \theta) \) could be in principle a non-unique minimizer for the function \( \hat{\phi} \), at fixed \( p \) and \( \theta \). However, in agreement with a classical point of view on crystal energies, let us suppose that, except for possibly isolated values of \( p \) and \( \theta \), \( \overline{C}(p, \theta) \) exists such that the stronger version

\[
\hat{\phi}(\overline{C}(p, \theta), p, \theta) < \hat{\phi}(C, p, \theta)
\]

of (4.8) holds for all \( C = C^T > 0 \), and all \( p, \theta \). This guarantees that \( \overline{C}(p, \theta) \) be a
unique surface of minimizers for \( \hat{R} \), satisfying the condition \( \overline{C}(p_0, \theta_0) = 1 \) because the reference configuration \( R \) picked above is itself a natural state of the crystal at room conditions, according to experimental observations.

Then, on account of (3.7), (4.9) yields

\[(4.10) \quad R^t \overline{C}(p, \theta) R = \overline{C}(p, \theta),\]

to hold for all rotations in the point group (1.9), and all admitted values of \( p \) and \( \theta \). Away from phase transitions, the geometrical symmetry does not change, so that the point group does not depend on \( p \) and \( \theta \).

By a well known theorem in linear algebra (see Truesdell [17, page 201]), (4.10) implies that the minimizing tensors \( \overline{C}(p, \theta) \) have the form

\[(4.11) \quad \overline{C}(p, \theta) = \gamma(p, \theta) I + \delta(p, \theta) E_3 \otimes E^3,\]

where \( \gamma \) and \( \delta \) are scalar valued functions on \( I \times J \) such that

\[(4.12) \quad \gamma(p_0, \theta_0) = 1, \quad \delta(p_0, \theta_0) = 0.\]

We thus conclude that once the reference state \( R \) above is picked, then the strain \( \overline{U}(p, \theta) \) of the minimizing deformations \( \chi = \chi(\chi, p, \theta) = \overline{F}(p, \theta) \chi \) is determined as follows:

\[(4.13) \quad \overline{U}(p, \theta) = \overline{C}^{1/2}(p, \theta) = \alpha(p, \theta) I + \beta(p, \theta) E_3 \otimes \overline{E}^3,\]

where \( \alpha = \sqrt{\delta} \), \( \beta = \sqrt{\delta + \delta - \sqrt{\delta}} \), and \( \alpha(p_0, \theta_0) = 1, \beta(p_0, \theta_0) = 0 \).

The meaning of the functions \( \alpha(p, \theta) \) and \( \beta(p, \theta) \) will became clear in sect. 6 below, but let us notice here that \( \alpha \) and \( \alpha + \beta \) describe the macroscopic changes in shape of the crystal in the reference configuration \( R \), as \( p \) and \( \theta \) vary within \( I \) and \( J \). Remembering that \( E_3 \) gives the direction of the optical axis of the hexagonal cell, and that \( E^3 = (1/c_0^2) E_3 \), (cf. (1.5)3) we see that the anisotropic compressibility and thermal expansion behaviour of quartz along that axis is accounted for by the function \( \beta \).

The rotation \( \overline{R} \) appearing in the polar decomposition \( \overline{F} = \overline{R} \overline{U} \) remains
arbitrary, according to galilean invariance. Notice that even letting \( \bar{R} \) depend on \( X \) to get \( D\bar{X}(X) = \bar{F}(X) = \bar{R}(X)\bar{U} \), a well known theorem in continuum mechanics assures that, under the continuity assumptions made here for \( \bar{X} \), \( R \) cannot depend on \( X \) and neither can \( \bar{F} \), so that no inhomogeneous deformations are obtained in this way.

Now that homogeneous natural states for a single homogeneous crystal have been described, we study a polycrystal composed of two joined individuals grown following the twinning law (2.1), and we render the form of its possible natural states explicit.

Let two homogeneous quartz crystals occupy two reference configurations \( R_1 \) and \( R_0 \) which are congruent and joined along a planar surface \( \Sigma_0 \) with normal \( N_0 \) oriented for instance as entering \( R_1 \). Letting \( R_0 \) be generated by the reference lattice vectors \( E_a \) (see (1.2)), and being \( R_0 \) (see (2.1)) the twinning operation, i.e. the rotation such that \( R_0R_0 = R_1 \), the vectors \( R_0E_a \) are then admissible lattice vectors for \( R_1 \). We recall that, according to (2.3), \( N_0 = E^1 + E^2 + -(2c_0/a_0)E^3 \).

The observations by CURIEN and KERN [13] and FRIEDLAENDER [15] support the idea that the reference configuration \( R = R_1UR_0 \) is itself a natural state (3) for the polycrystal at room temperature and pressure.

Since \( R \) is not homogeneous, the material response function depends on \( X \) besides \( C, p \) and \( \theta \) (see 4.7):

\[
\pi = \hat{\pi}(C, p, \theta, X) = \hat{\phi}(C, \theta, X) + pj.
\]

(4.14)

In consequence of (3.8), it is easily seen that whenever \( X(X) = FX \) is a homogeneous deformation of \( R = R_1UR_0 \) with \( C = F^tF \), then the following holds:

\[
\hat{\pi}(C, p, \theta, X) = \hat{\pi}(C, p, \theta) \quad \text{if} \quad X \in R_0,
\]

(4.15)

\[
\hat{\pi}(C, p, \theta, X) = \hat{\pi}(R_0^tCR_0, p, \theta) \quad \text{if} \quad X \in R_0R_0=R_1.
\]

where \( \hat{\pi}(C, p, \theta) \) is the response function appearing in (4.7).
We look for continuous, piecewise homogeneous deformations \( \mathbf{X} = \mathbf{X}(X, p, \theta) \) of \( R \) such that \( \mathbf{C}(X, p, \theta) = D\mathbf{X}^tD\mathbf{X} \) minimizes the ballistic free energy functional \( P[\mathbf{X}, p, \theta] \), the competitors being all the continuous, piecewise differentiable deformations \( \mathbf{\chi} \) of \( R \) in a suitable neighborhood of \( \mathbf{X}(X, p, \theta) \). The continuity of \( \mathbf{\chi} \) and \( \mathbf{X} \) expresses the notion that the parts of the whole polycrystal are firmly joined together, so that the body does not fracture. The piecewise homogeneous deformation \( \mathbf{X} \) above is given by:

\[
\mathbf{X}(X, p, \theta) = \mathbf{F}_i(p, \theta)X, \quad \text{for} \quad X \in R_i, \quad i = 0, 1,
\]

where \( \mathbf{F}_i \) are tensors in \( D \).

By galilean invariance, we can solve our problem up to rigid rotations of the whole twin, this being equivalent to the first of the conditions

\[
\mathbf{F}_0(p, \theta) = \mathbf{U}_0(p, \theta), \quad \mathbf{X}(X, p_0, \theta_0) = X,
\]

where \( \mathbf{U}_0 \) is symmetric and positive-definite. (4.17) holds as a consequence of (4.17) and of the fact that \( R \) is itself a natural state for \( p = p_0, \theta = \theta_0 \).

To render the deformation \( \mathbf{X}(X, p, \theta) \) defined by (4.16-17) explicit, suppose \( \mathbf{X} \) is such that, for every fixed value of \( p \) and \( \theta \), the minimizing condition

\[
\int_R \hat{P}[C(X), p, \theta, X]dX \geq \int_R \hat{P}[\mathbf{C}(X, p, \theta), p, \theta, X]dX
\]

(with \( \mathbf{C}(X, p, \theta) = D\mathbf{X}^t(X, p, \theta)D\mathbf{X}(X, p, \theta) \)) holds for all continuous piecewise differentiable deformations \( \mathbf{\chi}(X) \) with \( C(X) = D\mathbf{\chi}^tD\mathbf{\chi} \) in a suitable neighborhood of \( \mathbf{C}(X, p, \theta) = D\mathbf{X}^tD\mathbf{X} \).

By defining as usual \( \mathbf{C}_i = \mathbf{F}_i^t \mathbf{F}_i \) (not summed, \( i = 0, 1 \)), and on account of (4.15-16), the inequality (5.18) becomes explicitly:

\[
\int_{R_0} \hat{P}[C(X), p, \theta]dX + \int_{R_1} \hat{P}[R_0^tC(X)R_0, p, \theta]dX \geq \int_{R_0} \hat{P}[\mathbf{C}_0(p, \theta), p, \theta]dX + \int_{R_1} \hat{P}[R_0^t\mathbf{C}_1(p, \theta)R_0, p, \theta]dX.
\]
Now introduce, for fixed negative $\varepsilon$, a planar surface $\mathcal{A}_\varepsilon = \{ \mathbf{x} \in R_0 : \mathbf{x} \cdot \mathbf{N}_0 = \varepsilon \}$. $\mathcal{A}_\varepsilon$ is parallel to the contact plane $\mathcal{A}_0$, so that the region $R_0$ is divided into two subsets: the layer $\mathcal{L}_\varepsilon = \{ \mathbf{x} \in R_0 : \varepsilon \leq \mathbf{x} \cdot \mathbf{N}_0 \leq 0 \}$ and the complementary part $R_0^- \setminus \mathcal{L}_\varepsilon$.

Let $C$ be an arbitrary, symmetric, positive-definite tensor, and define the function $\chi_\varepsilon$ as follows:

$$
\chi_\varepsilon^{1/2} \chi \begin{cases} 
(1/\varepsilon) ((\varepsilon - \mathbf{x} \cdot \mathbf{N}_0) \mathcal{C}_1(p, \theta)^{1/2} \mathbf{x} + \mathbf{x} \cdot \mathbf{N}_0 \mathcal{C}^{1/2} \mathbf{x}) & \text{if } \mathbf{x} \in R_0^- \setminus \mathcal{L}_\varepsilon, \\
\mathcal{C}_1(p, \theta)^{1/2} \mathbf{x} & \text{if } \mathbf{x} \in \mathcal{L}_\varepsilon, \\
\mathcal{C}_1(p, \theta)^{1/2} \mathbf{x} & \text{if } \mathbf{x} \in R_1.
\end{cases}
$$

The deformation $\chi_\varepsilon$ defined in (5.20) is continuous and piecewise differentiable. Hence it is an allowable competitor for the minimizing problem (4.18) or (4.19).

The substitution of $\chi_\varepsilon$ for $\chi$ into (4.19) yields ($\mathcal{C}_\varepsilon(\mathbf{x}) = D\chi_\varepsilon^t D\chi_\varepsilon$):

$$
\int_{R_0^- \setminus \mathcal{L}_\varepsilon} \mathbf{\hat{p}}(\mathbf{c}, p, \theta) d\mathbf{x} + \int_{R_1} \mathbf{\hat{p}}(\mathbf{R}_0^t \mathcal{C}_1(p, \theta) \mathbf{R}_0, p, \theta) d\mathbf{x} + \int_{\mathcal{L}_\varepsilon} \mathbf{\hat{p}}[\mathcal{C}_\varepsilon(\mathbf{x}), p, \theta] d\mathbf{x} \geq
$$

$$
\int_{R_0} \mathbf{\hat{p}}(\mathcal{C}_0(p, \theta), p, \theta) d\mathbf{x} + \int_{R_1} \mathbf{\hat{p}}[\mathbf{R}_0^t \mathcal{C}_1(p, \theta) \mathbf{R}_0, p, \theta] d\mathbf{x}.
$$

The inequality above holds for all $\mathbf{C}$ in a neighborhood of $\mathcal{C}_0(p, \theta)$, and for all $\varepsilon$ in a left neighborhood of zero.

In our hypotheses, we see that $\lim_{\varepsilon \to 0} \int_{\mathcal{L}_\varepsilon} \mathbf{\hat{p}}[\mathcal{C}_\varepsilon(\mathbf{x}), p, \theta] d\mathbf{x} = 0$, and hence, in the limit of vanishing $\varepsilon$, (4.21) gives

$$
\mathbf{\hat{p}}(\mathbf{c}, p, \theta) \geq \mathbf{\hat{p}}(\mathcal{C}_0(p, \theta), p, \theta),
$$

an inequality which holds for all $\mathbf{C}$, near $\mathcal{C}_0(p, \theta)$. This means that $\mathcal{C}_0(p, \theta)$ fulfills (4.19) if and only if it is a minimizer for $\mathbf{\hat{p}}$. Furthermore, by (4.17)$_2$, $\mathcal{C}_0(p, \theta_0) = 1$, so that $\mathcal{C}_0(p, \theta)$ has to coincide with the (unique)
surface of minimizers $\overline{C}(p, \theta) = \gamma 1 + \delta E_3 \otimes E^3$ found above. Hence

$$\overline{C}_0(p, \theta) = \overline{C}(p, \theta) = \gamma 1 + \delta E_3 \otimes E^3.$$  

(4.23)

(4.19) and (4.23) imply that also $R_0^t \overline{C}_1(p, \theta) R_0$ must be a minimizer for $\overline{\Gamma}$, and again by (4.17)_2, it is $R_0^t \overline{C}_1(p_0, \theta_0) R_0 = 1$. Thus:

$$R_0^t \overline{C}_1(p, \theta) R_0 = \overline{C}(p, \theta) = \gamma 1 + \delta E_3 \otimes E^3.$$  

(4.24)

whence

$$\overline{C}_1(p, \theta) = R_0^t \overline{C}_0(p, \theta) R_0^t.$$  

(4.25)

and it is therefore proved that the polycrystal can be in a natural state if and only if both the composing crystals are themselves in natural states. Furthermore, equation (4.25) implies that while the twin $R$ is deformed, the lattice belonging to each of the differently oriented individuals $R_1$ accordingly deforms necessarily "in the same way" with respect to each set of lattice vectors $R_0^i E_a$, $i=0,1$.

Equation (4.25) is equivalent to:

$$\overline{F}_1(p, \theta) = R(p, \theta) \overline{F}_0(p, \theta) R_0^t.$$  

(4.26)

where $R(p, \theta)$ is a suitable function which has the meaning of relative rotation of the two deformed twinned individuals. Thus, $R(p, \theta)$ is the twinning operation at the various temperatures and pressures, and in this way it turns out to be sensitive to the environmental conditions in the growth-site. We will see it is uniquely determined by the requirement that $\overline{\Gamma}$ be continuous. Equation (4.17)_2 implies

$$R(p_0, \theta_0) = R_0.$$  

(4.27)

Having determined the tensors $\overline{C}_i(p, \theta)$ in (4.23) and (4.25), we proceed to write the deformation gradients $\overline{F}_i(p, \theta)$, for $i=1,2$, explicitly as follows (see (4.16), (4.17)_1, (4.13) and (4.26)): 

16
\[ F_0(p, \theta) = \overline{C}^{1/2}(p, \theta) = \overline{U}(p, \theta) \]

(4.28)

\[ F_1(p, \theta) = R(p, \theta)\overline{U}(p, \theta)R_0^t. \]

At this stage, the twinning operation \( R(p, \theta) \) is unknown. It is determined by solving the following equation of compatibility:

(4.29) \[ \overline{F}_1(p, \theta) - \overline{F}_0(p, \theta) = a(p, \theta) \otimes N_0. \]

This is a necessary condition for the deformation defined by (4.16) and (4.17) to be continuous in \( \mathbf{X} \) for all \( p \) and \( \theta \). In (4.29), \( a(p, \theta) \) is an unknown vector function of \( p \) and \( \theta \), and \( N_0 \) is the normal to the contact plane \( \mathbf{S}_0 \).

Once the vector \( \mathbf{A}(p, \theta) = \overline{U}^{-1}a \) is introduced, (4.29) can be rewritten as

(4.30) \[ R(p, \theta)\overline{U}(p, \theta)R_0^t = \overline{U}(p, \theta)[1 + \mathbf{A}(p, \theta) \otimes N_0]. \]

Taking the determinant of both sides of (4.30), it is easily seen that \( A \cdot N_0 = 0 \) whence \( 1 + A \otimes N_0 \) is a simple shear. Furthermore, since \( \overline{U}(p_0, \theta_0) = 1 \) and \( R(p_0, \theta_0) = R_0 \), (4.30) gives \( 1 + A(p_0, \theta_0) \otimes N_0 = 1 \), which is true if and only if \( A(p_0, \theta_0) = 0 \), which in turn implies \( a(p_0, \theta_0) = 0 \).

Omitting the details, we can show that if the vectors \( \mathbf{e}_a(p, \theta) = \overline{U}(p, \theta)\mathbf{e}_a \) are defined, the unique solution of equation (4.30) is the rotation \( R(p, \theta) \) given by

\[ R(p, \theta)e_a = R_a^b e_b, \] with

(4.31) \[ R_a^b = \left[ ((\alpha + \beta)^2 + \alpha^2)^{-1} \right]^{-1} \left[ \begin{array}{ccc} \alpha^2 & -(\alpha + \beta)^2 & \alpha^2a_0/c_0 \\ -(\alpha + \beta)^2 & \alpha^2 & \alpha^2a_0/c_0 \\ -2c_0(\alpha + \beta)^2/a_0 & -2c_0(\alpha + \beta)^2/a_0 & (\alpha + \beta)^2 - \alpha^2 \end{array} \right]. \]

where \( \alpha \) and \( \beta \) are the quantities introduced in (4.13).

The role of the vectors \( \mathbf{e}_a(p, \theta) \) will be discussed below in sect. 6, but we anticipate here that they can be given the meaning of lattice vectors of the quartz hexagonal cell in the deformed configuration. In this way, the rotation axis of \( R(p, \theta) \) turn out to be the crystallographic row given by
\[ e_2 - e_1 = \overline{U}(E_2 - E_1) \] in the deformed crystal, and calling \( \psi \) the twinning angle, we find \( \cos \psi = -[(\alpha + \beta)^2 - \alpha^2]/[(\alpha + \beta)^2 + \alpha^2] \), so that \( \psi \) departs from \( \pi/2 \) as soon as \( \beta \) is different from zero (cf. footnote 3).

It is also worth noting that the "reference" contact plane \( \mathcal{A}_0 \) behaves as a material plane in consequence of the assumptions made above. The interface \( \mathcal{A}(p, \theta) = \mathcal{A}(\mathcal{A}_0, p, \theta) \) in the deformed configuration has normal direction given by
\[ \mathbf{N}(p, \theta) = \overline{U}^{-1}(p, \theta) N_0 = e^1 + e^2 - 2(c_0/a_0)e^3, \]
and thus maintains the same indices independently of \( p \) and \( \theta \): it always passes through the "same" lattice points.

The amplitude vector \( A(p, \theta) \) is given by:

\[ (4.32) \quad A(p, \theta) = \frac{1}{2} \left[ \left( \frac{(\alpha + \beta)^2 - \alpha^2}{(\alpha + \beta)^2 + \alpha^2} \right) \left[ E_1^* E_2^* (a_0/c_0) E_3 \right] \right]. \]

The condition that \( R(p, \theta) \overline{U}(p, \theta) R_0^t x = \overline{U}(p, \theta) x \) for all \( x \in \mathcal{A}_0 \) implies that the solution \( R(p, \theta) \) of (4.30) is necessarily unique. Substitution of \( R(p, \theta) \) into (4.28), together with condition (4.17) determine (up to unessential rigid rotations of the whole body) the surface \( x = \overline{x}(x, p, \theta) \) sought for twin natural states.

### 5. Crosses. Geobarothermometric implications

We are now in position to handle our original problem, i. e. to model the behaviour of some of the crystalline formations reported by FRIEDLAENDER [15]: quartz "crosses" whose twinning operation is given by (2.1).

As already mentioned in sect. 2, \( R_0 \) is a period 4 operation. Hence, considering a reference configuration \( R_0 \) for a quartz crystal (an "arm" of the cross) generated by the reference lattice vectors \( E_a \) introduced in (1.2), we get the three other congruent arms operating on \( R_0 \) by the various powers \( R_0^i \) of \( R_0 \): \( R_i = R_0^i R_0 \). \( R_i \) is generated of course by the lattice vectors \( R_0^i E_a \), \( i=0,1,2,3 \). This extends the procedure adopted in the case of the twin pair analyzed in the preceding section. We assume that planar surfaces \( \mathcal{A}_i \) with normal directions \( N_i = R_0^i N_0 \) (see (2.3)) have been suitably cut on the
various $R_i$, and that they are joined along the surfaces $\&_i$ as indicated in
fig. 1 to give $R = UR_i = U R_0 i R$.

$R$ is picked as reference configuration for the cross, and we assume that it
is a natural state for the polycrystal at room temperature and pressure.
This agrees with the observation of the specimen reported in [15, fig. 4]
(cf. footnote (3)).

Notice that
\begin{equation}
N_0 = - N_2, \quad \text{and} \quad N_1 = - N_3.
\end{equation}

The determination of the continuous, piecewise homogeneous stable stress-
free equilibria $\chi = \chi(X, p, \theta)$ is now analogous to the case discussed in the preceding section.

By the same procedure adopted there, in fact, we find that a continuous
piece-wise homogeneous deformation $\chi = \chi(X, p, \theta)$ defined by
\begin{equation}
\chi(X, p, \theta) = \bar{F}_i(p, \theta)X, \quad \text{for} \quad X \in R_i, \quad i = 0, 1, 2, 3,
\end{equation}
with
\begin{equation}
\bar{F}_0(p, \theta) = \bar{U}_0(p, \theta), \quad \bar{U}_0 = \bar{U}_0^t > 0, \quad \chi(X, p_0, \theta_0) = X, \quad \bar{c}_i = \bar{F}_i^t \bar{F}_i.
\end{equation}

locally minimizes the total ballistic free energy functional for the joined
body if and only if the tensors $\bar{c}_i(p, \theta)$ are such that the following inequa-
\begin{equation}
\sum \int_{R_i} \{ \bar{F}[R_0 i]^t D \chi^t(D \chi)(X) R_0 i, p, \theta] - \bar{F}[R_0 i]^t \bar{c}_i(p, \theta) R_0 i, p, \theta \} dX \geq 0
\end{equation}
holds for all continuous, piecewise differentiable deformations $\chi$ of $R$ and
belonging to suitable neighborhoods of $\chi(X, p, \theta)$ for all fixed $p, \theta$ in $I$ and $J$
respectively. (5.4) corresponds to the preceding (4.19).

It is not difficult to show that the same kind of reasoning, leading from
(4.19) to (4.23) and (4.25) can be applied now to (5.4), and we prove in
this way that (5.4) holds if and only if
\begin{equation}
\bar{c}_0(p, \theta) = \bar{c}(p, \theta) = \bar{U}^2 = \gamma 1 + \delta E_3 \otimes E_3, \quad \text{and} \quad \bar{c}_i = R_0 i \bar{c}_0(p, \theta)(R_0 i)^t.
\end{equation}
i = 1, 2, 3. Hence, by (5.3)$_1$ and (5.5)$_4$ we get

\begin{equation}
(5.6) \quad \bar{F}_0(p, \theta) = \bar{U}(p, \theta), \quad \text{and} \quad \bar{F}_i = R_i(p, \theta) \bar{U}(p, \theta) (R_0^t)^i, \quad \text{for} \ i = 1, 2, 3.
\end{equation}

The remarks made below equation (4.25) apply now, too: the rotations $R_i(p, \theta)$ above are not yet known.

In the present case, compatibility of the gradients imposes that the four following equations hold:

\begin{align}
\bar{F}_1 - \bar{F}_0 &= a_0 \otimes N_0, & \bar{F}_2 - \bar{F}_1 &= a_1 \otimes R_0 N_0, \\
\bar{F}_3 - \bar{F}_2 &= a_2 \otimes R_0^2 N_0, & \bar{F}_0 - \bar{F}_3 &= a_3 \otimes R_0^3 N_0,
\end{align}

\begin{equation}
(5.7)
\end{equation}

where the arguments are omitted. Here, the $a_i$ are unknown vectors that depend on $p$ and $\theta$.

With $\bar{F}_0$ given by (5.6)$_1$, and with $A_0 = \bar{U}^{-1} a_0$, (5.7)$_1$ becomes the same as (4.29), which has already been solved, and this in turn completely determines the solution of equations (5.7)$_2, 3, 4$, as we now show.

Let us indicate here with $R_i(p, \theta)$ and $A_0(p, \theta)$ the solutions of (5.7)$_1$ which coincide with the solutions $R(p, \theta)$ and $A(p, \theta)$ of (4.29) found above (see (4.31) and below).

On account of (5.3)$_1$ and (5.6)$_1$, (5.7)$_2$ becomes

\begin{equation}
(5.8) \quad R_2(p, \theta) \bar{U}(p, \theta) (R_0^t)^2 - R_1(p, \theta) \bar{U}(p, \theta) R_0^t = a_1(p, \theta) \otimes R_0 N_0.
\end{equation}

Right multiplication by $R_1^t$ and left multiplication by $R_0$, yield

\begin{equation}
(5.9) \quad R_1^t R_2 \bar{U} R_0^t = \bar{U} + R_1^t a_1 \otimes N_0,
\end{equation}

which is an equation (in the unknown rotation $R_1^t R_2$ and vector $R_1^t a_1$) that coincides with (4.30). Uniqueness of the solutions of this equation then gives

\begin{equation}
(5.10) \quad R_1^t R_2 = R_1, \quad R_1^t a_1 = a_0,
\end{equation}

namely
(5.11) \[ R_2(p, \theta) = R_1^2(p, \theta), \quad a_1(p, \theta) = R_1(p, \theta)a_0(p, \theta), \]

as solutions of (5.7)_2. Analogous procedure leads to the solutions of equation (5.7)_3 as follows:

(5.12) \[ R_3(p, \theta) = R_1^3(p, \theta), \quad a_2(p, \theta) = R_1^2(p, \theta)a_0(p, \theta). \]

Finally, equation (5.7)_4 can be written

(5.13) \[ \bar{U} - R_3 \bar{U}(R_0^3)^t = a_3 \otimes R_0^3 N_0, \]

or also, remembering that \( R_0^3 = R_0^t \):

(5.14) \[ R_3^t \bar{U} R_0^t - \bar{U} = R_3^t a_3 \otimes N_0, \]

which is again of the same type as (4.30). Hence

(5.15) \[ R_3^t = R_1, \quad R_3^t a_3 = a_0, \quad \text{whence} \quad R_3 = R_1^t, \quad a_3 = R_1^t a_0. \]

Now, by eliminating the F's from equations (5.7) the following condition is obtained:

(5.16) \[ a_0 \otimes N_0 + a_1 \otimes R_0 N_0 + a_2 \otimes R_0^2 N_0 + a_3 \otimes R_0^3 N_0 = 0, \]

which, by (5.1), (5.12)_2, (5.13)_3 and (5.14), becomes

(5.17) \[ (a_0 - R_1^2 a_0) \otimes N_0 + (R_1 a_0 - R_1^t a_0) \otimes R_0 N_0 = 0. \]

This must hold for all \( p \) and \( \theta \).

With the given data, \( N_0 \) and \( R_0 N_0 \) are independent vectors, so that (5.17) holds if and only if

(5.18) \[ a_0 = R_1^2 a_0 \]

As it is easy to see, this can be true if and only if
(5.19) \[ a_0(p, \theta) = 0 \]

for all \( p \) and \( \theta \). In fact \( a_0 \) is not parallel to \( R_1 \)'s axis; it is indeed orthogonal to it, as shown by (4.31-32) and (4.13). The identity (5.19) also implies that \( a_i(p, \theta) = 0 \) for all \( p \) and \( \theta \) \((i=1,2,3)\), and it is furthermore equivalent to each of the following others:

(5.20) \[ \beta(p, \theta) = 0, \quad R_1(p, \theta) = R_0. \]

In fact (5.20)_1 follows at once from (5.19), (4.13)_4 and (4.32), whereas (5.20)_2 is a consequence of (5.20)_1, (4.13) and (4.30-31).

We thus proved that a necessary and sufficient condition for the quartz cross to be in a natural state is that any of the three equivalent equations (5.19), (5.20)_1 or (5.20)_2 be identically satisfied in \( p \) and \( \theta \), so that only a path of natural states is found in this case. Equations (5.19) or (5.20) immediately imply that each arm of the cross maintains itself in a natural state. Equation (5.20)_1 is the most important, and it is the basis of the geobarothermometric properties of these formations.

As discussed in the Introduction, in fact, only when this equation is satisfied, does the environment provide the best circumstances for the polycrystal to grow. On the contrary, growth-sites whose evolution is described by parameters \( p \) and \( \theta \) with values which are not at least near the graph of equation (5.20)_1, either would not be favorable for the growth of the crystal in the given cross shape, or would lead the grown formation to a condition in which the stress created might cause the polycrystal to fracture.

The presence of crystals exhibiting special twinned shapes is hence to be interpreted as a sign that a particular path has been followed by the growth-site parameters, and the history of the material can hence be estimated; in the present case this is given by the graph of equation \( \beta(p, \theta) = 0 \). This also gives the best conditions for artificial growth.

In principle, the same general kind of thermoelastic model used here to describe the behaviour of growth twins, can be applied to a large class of
more general and complex crystalline edifices, for instance to regular associations of crystals of possibly different species (epitaxial intergrowths). The purpose of analyzing these formations is to deliver the same kind of information regarding the growth-sites as we obtained now for quartz crosses; what is useful for this is the theory developed by Ericksen [31] and James [32], because growth twins, as modeled here, turn out to be a special case of the "stress-free" joint bodies introduced in these papers. Thus we have the beginning of a new mineralogic technique of quantitative geobarothermometry, based on morphological study of polycrystalline bodies, provided some data are known about the crystals involved.

6. An assessment of the behavior of low quartz lattice-parameters. Temperature-dependent Thurston equations and explicit determination of the barothermometric path \( \beta(p, \theta) = 0 \).

It is now interesting to determine explicitly the graph of the equation \( \beta(p, \theta) = 0 \). To interpret most of the available experimental data, we need to relate the macroscopic and molecular descriptions, that is, we have to establish a relation between the macroscopic deformation of the crystal and the atomic movements.

For the kind of phenomena studied in this work, we already made the assumption not to consider the shuffle movements of atoms (such as are discussed by Pitteri [25]). We use the classical rule due to Cauchy and Born, as it is interpreted for instance by Ericksen [19]: when the body undergoes a homogeneous deformation \( \chi = \chi(X) = FX \) (\( F = \text{const} \)) starting from a reference configuration whose lattice vectors are \( E_a \), then the vectors \( e_a \) defined by

\[
(6.1) \quad e_a = FE_a
\]

constitute a possible set of lattice vectors for the (homogeneously) deformed configuration \( (4) \).

Hence, the vectors

\[
(6.2) \quad e_a(p, \theta) = \bar{U}(p, \theta)E_a = [\alpha(p, \theta)1 + \beta(p, \theta)E_3 \otimes E_3]E_a
\]

have in our case the meaning of lattice vectors for low-quartz when the external pressure and temperature are \( p \) and \( \theta \) respectively (see below.
(4.13) and below (4.30)). Then setting as usual \( a(p, \theta) = (e_i \cdot e_1)^{1/2} \) for \( i = 1, 2, \) and \( c(p, \theta) = (e_3 \cdot e_3)^{1/2} \), we get

\[
(6.3) \quad \alpha = a(p, \theta)/a_0, \quad \alpha + \beta = c(p, \theta)/c_0 ,
\]

that is, the functions \( \alpha \) and \( \alpha + \beta \) are the lattice-parameters ratios as \( p \) and \( \theta \) vary within \( I \) and \( J \).

As already mentioned above, the anisotropic compressibility and thermal expansion behaviour of quartz along the optical axis is accounted for by the function \( \beta(p, \theta) \).

Even though quartz is a most-studied material, the exact kind of data needed here, i.e. experimental measurements of the combined effect of both \( p \) and \( \theta \) on the crystal parameters, have not been determined yet. In fact, we did not find much in the literature concerning the explicit form of the functions \( \alpha \) and \( \alpha + \beta \).

In principle, these data can be obtained by means of the experimental procedures initiated in the 20's by Bridgman (see for instance [33], [34]). A great deal of data has been collected in this way for the ratios \( \alpha(p, \theta_0) \) and \( \alpha(p, \theta_0) + \beta(p, \theta_0) \), which describe the isothermal changes with pressure of the lattice parameters, or also, the change with pressure of the isothermal linear compressibility in the various directions of the lattice unit cell, at room temperature: see for instance LeVien et al. [8], Jorgensen [9], Bridgman [33], [34], D'Amour et al. [35], Vaidya et al. [36], Mc Whan [37], Olinger [38], Taylor [39]. Of course, for symmetry reasons, only two directions are important in low-quartz: the one which is parallel to the optical axis, and the one orthogonal to it. Also the functions \( \alpha(p_0, \theta) \) and \( \beta(p_0, \theta) \), which account for the thermal expansion of the crystal at atmospheric pressure are rather well known, see for instance Taylor [39], Jay [40], Berger et al. [41], Ackermann and Sorrell [42].

However, the most abundant are data for the isothermal bulk compressibility of quartz at room temperature, i.e. data on the isothermal volume variations of a given sample of material as function of \( p \), for \( \theta = \theta_0 \). In our notations this is described for quartz by a function
(6.4) \[ V(p, \theta_0) = \overline{J}(p, \theta_0)V_0 = \alpha^2(p, \theta_0)[\alpha(p, \theta_0) + \beta(p, \theta_0)]V_0 \]

where \( V_0 \) is the volume of the reference configuration (usually picked as the natural state at \( p=p_0, \theta=\theta_0 \)), and where \( \overline{J}(p, \theta) = \det \overline{U}(p, \theta) \), \( \overline{U}(p, \theta) \) being the locally unique surface of natural states (4.13) issuing from \( \overline{U}(p_0, \theta_0)=1 \).

With the compression experiments performed at constant (room) temperature, the effect of the external pressure on the volume can be empirically described in various ways, depending on the pressure interval one is interested in.

In most of his work, BRIDGMAN uses a quadratic polynomial in \( p \) (cf. [34]):

(6.5) \[ V = V_0(Ap + Bp^2) \]

where the quantities \( A \) and \( B \) are functions of \( \theta \).

Note that we will henceforth put \( p_0=0 \), as is usual within the range of pressures considered below.

Extrapolation formulas other than (6.5) are discussed by ANDERSON [43]: a very useful one is given by the BIRCH equation (see BIRCH [44], [45], or also D'AMOUR et al. [35], MC WHAN [37]). However, the non-polynomial formula which is by far the most widely used is known as the MURNAGHAN equation (see for instance MURNAGHAN [46] or ANDERSON [43]).

To briefly illustrate it and the hypotheses upon which it is based, let an undistorted reference configuration \( R \) be picked for the solid, and let us consider the minimizers \( U = \overline{U}(p, \theta) \) as we did in introducing the function \( V=V(p, \theta) \) above.

With \( \overline{J}(p, \theta) = \det \overline{U}(p, \theta) \), we define the isothermal bulk compressibility \( K(p, \theta) \) and the isothermal bulk modulus \( B(p, \theta) \) as follows:

(6.6) \[ K = \overline{J}_p / \overline{J}, \quad B = 1/K = -V/V_p. \]

MURNAGHAN's assumption is that \( B(p, \theta) \) is a linear function of the pressure:

(6.7) \[ B(p, \theta) = B_0(\theta) + B_0'(\theta)p. \]

Here, \( B_0(\theta) = B(p_0, \theta) \) is the bulk modulus evaluated at room pressure,
whereas $B'_0(\theta) = B_p(p, \theta) = B_p(p_0, \theta)$ is the first pressure-derivative of $B(p, \theta)$, which, by assumption, is independent of $p$.

By (6.6), equation (6.7) can be interpreted as a differential equation in the unknown function $V(p, \theta)$, which is immediately integrated to give:

\[
V(p, \theta) / V(p_0, \theta) = [1 + pB'_0(\theta)/B_0(\theta)]^{-1/B_0'(\theta)}.
\]

For $\theta = \theta_0$, (6.8) becomes the extrapolation formula proposed by Murnaghan in [46]. It does fit the room temperature compression data well enough for most solids up to the highest pressures (see for instance LeVien et al. [8], Jorgensen [9], Vaidya [36], Mc Whan [37], Anderson [43], Murnaghan [46]).

Quadratic polynomial expressions similar to (6.5) were also used by Bridgman to fit the isothermal linear compression data he obtained, i.e., data for the functions $\alpha(p, \theta_0)$ and $\beta(p, \theta_0)$. As is discussed by Taylor [39], for example, fourth-power polynomial fittings are available for them, too. The only non-polynomial assessment of the form of the functions $\alpha(p, \theta_0)$ and $\beta(p, \theta_0)$ has been tried by Thurston [47], rather recently. He gave, in fact, extrapolation formulas for the principal stretches (i.e., for the eigenvalues of $\Sigma(p, \theta_0)$) which are based on substantially the same assumptions as Murnaghan's. In detail, let

\[
\alpha(p, \theta) = \alpha(p_0, \theta)[1 + A_1 p + \frac{1}{2} B_1 p^2 + ...],
\]

\[
\alpha(p, \theta) + \beta(p, \theta) = [\alpha(p_0, \theta) + \beta(p_0, \theta)][1 + A_3 p + \frac{1}{2} B_3 p^2 + ...].
\]

be the $p$-power series expansions of the stretches $\alpha$ and $\alpha + \beta$, where the coefficients $A_1$, $A_3$, $B_1$, $B_3$ are functions of $\theta$ only. Truncating these expressions at the quadratic terms gives poor fits at high pressures. First, Thurston obtained the following relation for the pressure derivative of the bulk modulus:

\[
B_p(p, \theta) = 2B^2(p, \theta) \gamma_1(p, \theta) + B^2(p, \theta) \gamma_2(p, \theta),
\]

where
\[ Y_1(p, \theta) = \alpha^{-1} \alpha_{pp} - \alpha^{-2}(\alpha_p)^2 \]

(6.11)

\[ Y_3(p, \theta) = (\alpha + \beta)^{-1}(\alpha + \beta)_{pp} - (\alpha + \beta)^{-2}[(\alpha + \beta)_p]^2. \]

As Murnaghan assumed the derivative \( B_p \) to be a function of the temperature only (cf. [46] or (6.7)), the derivation of the extrapolation formulas in [47] is similarly based on the assumption that each term of the addition in the l. h. s. of (6.10) be a function of \( \theta \) only, so that, by means of (6.9), Thurston found the following relations (6.12):

\[ B^2(p, \theta)Y_1(p, \theta) = B^2(p_0, \theta)[B_1(\theta) - A_1^2(\theta)]. \]

(6.12)

\[ B^2(p, \theta)Y_3(p, \theta) = B^2(p_0, \theta)[B_3(\theta) - A_3^2(\theta)]. \]

By (6.10), equations (6.12)_{1,3} imply, of course, that \( B_p \) is independent of \( p \), so that (6.7) holds, too.

By (6.6), (6.7) and (6.11), equations (6.12)_{1,2} are interpreted as second order differential equations in the unknown functions \( \alpha \) and \( \alpha + \beta \); a double integration yields:

\[ \alpha = \alpha(p_0, \theta) [1 + pB'_0(\theta)/B_0(\theta)] H_1(\theta) \cdot \exp \{K_1(\theta)p\} \]

(6.13)

and

\[ \alpha + \beta = [\alpha(p_0, \theta) + \beta(p_0, \theta)][1 + pB'_0(\theta)/B_0(\theta)] H_3(\theta) \cdot \exp \{K_3(\theta)p\}. \]

(6.14)

where for brevity we have set

\[ H_i(\theta) = -B_0^{-2}(\theta)[B_i(\theta) - A_i^2(\theta)]/B_0^{-2}(\theta) \]

and

\[ K_i(\theta) = A_i(\theta) + (B_0(\theta)[B_i(\theta) - A_i^2(\theta)]) / B_0'(\theta). \]

For \( \theta = \theta_0 \), these are Thurston's equations. Their use is commonly based on low-pressure, room-temperature estimates of the material parameters \( A_1, A_3, B_1, B_3, B_0, B'_0 \), and they prove to fit room-temperature, high-pressure linear compression data very well for a great number of solids (see for instance Levi en et al. [8], Jorgensen [9], Mc Whan [37], Olinger and Halleck.
[38], Thurston [47]).
The fit is very good for quartz (at \( \theta = \theta_0 \)) up to about \( 70 \times 10^8 \) Pa [38], or at least up to pressures two orders of magnitude higher than the ones used for the parameter estimates, according to [37].
Since (6.7) holds, it is easily seen that the Murnaghan equation (6.8) follows from equations (6.13-14).

Two attempts to fully describe the function \( V = V(p, \theta) \) for solids are made in very recent papers by Hosieni et al. [48], and Fernandez Guillermet and Gustafson [49]. By a careful analysis of all the available experimental data, the authors gave in [48] the coefficients of a 35-term polynomial expansion of \( V(p, \theta) \) for \( \text{SiO}_2 \) in its various phases, whereas in [49] a non-polynomial expression of \( V(p, \theta) \) is given for iron. In [49], the functional form of \( V(p, \theta) \) is achieved by a temperature-correction of the Murnaghan equation: the dependence upon temperature of some of the parameters appearing in (6.8) is in fact introduced for the first time. According to the authors, the equation obtained in this way accounts satisfactorily for the properties of the various phases of condensed iron, although the lack of experimental data was in some cases considerable, and forced the use of systematic linear approximation to most of the functions involved.

Nothing analogous to the work done in [48] and [49] for \( V(p, \theta) \), could be found in the literature about the ratios \( \alpha \) and \( \alpha + \beta \) of interest to us.
Here, we follow the lead of [49] and modify the Thurston equations by considering the temperature dependence of the parameters \( A_1, A_3, B_1, B_3, B_0, B'_0 \) appearing in (6.13-14).

Measures of the linear compressibility of quartz vs. pressure at various temperatures are almost totally lacking. The only data we found are in Bridgman's work [34], where the linear compression measures are reported for quartz samples up to pressures of about 12 kbar and at two distinct temperatures: \( \theta_0 = 30^\circ \text{C} \), and \( \theta = 75^\circ \text{C} \).
The data collected in [34] only allow for a linear estimate of the temperature dependence of \( A_1, A_3, B_1, B_3, B_0, B'_0 \), since they refer to two different temperatures only.
The linear extrapolations are the following, with \( \theta_0 = 30^\circ \text{C} \) (we will henceforth express \( \theta \) in °C and \( p \) in kbar):

28
\[10^4 A_1(\theta) = -10.015 - 0.00362 (\theta - \theta_0),\]
\[10^6 B_1(\theta) = 20.52 + 0.0042 (\theta - \theta_0),\]
\[10^4 A_3(\theta) = -6.247 - 0.00357 (\theta - \theta_0),\]
\[10^6 B_3(\theta) = 15.8 + 0.0302 (\theta - \theta_0),\]
\[B_0(\theta) = 366 - 0.133 (\theta - \theta_0),\]
\[B_0'(\theta) = 5.95 - 0.0016 (\theta - \theta_0).\]

(6.15)

As shown by Anderson [43, eqs. (2) and (15)], the quantities \(B_0\) and \(B_0'\) are related to the coefficients \(A\) and \(B\) appearing in (6.5) as follows:

\[B_0(\theta) = -\frac{1}{A(\theta)}, \quad B_0'(\theta) = -1 + \frac{2B(\theta)}{A^2(\theta)}.\]

(6.16)

These equations together with Bridgman's [34] data for \(A\) and \(B\) gave the linear functions (6.15).

The bulk modulus \(B_0\) and its first pressure derivative \(B_0'\) turn out to have the room temperature values of 366 kbar and of 5.95 respectively, which are in remarkably good agreement with the most recent determinations, see Levien et al. [8, table 6]. Also the room temperature values of the parameters \(A_1\), \(A_3\), \(B_1\) and \(B_3\) turns out to agree well with the estimates given for instance by Mc Whan [37] and Thurston [47], except for \(B_1\) that Bridgman finds about 20% higher.

It is not possible to make an a priori judgement about the range of temperatures in which the linear approximations (6.15) are good; notice anyway that to obtain them, Bridgman's [34] data have been corrected according to Rotter and Smith [50] (of course the figures reported in [34] have been further corrected because of the different units for pressure used here).

Let us also consider the following fourth-power polynomial expansions for the functions \(\alpha(p_0, \theta)\) and \(\alpha(p_0, \theta) + \beta(p_0, \theta)\), as they are reported in the review article by Taylor [39, table 1]:

\[\alpha(p_0, \theta) = 1 + 1.354 \times 10^{-5} \theta + 1.18 \times 10^{-8} \theta^2 - 1.7 \times 10^{-11} \theta^3 + 4.4 \times 10^{-14} \theta^4,\]

(6.17)
\[\alpha(p_0, \theta) + \beta(p_0, \theta) = 1 + 0.733 \times 10^{-5} \theta + 0.86 \times 10^{-8} \theta^2 - 1.01 \times 10^{-11} \theta^3 + 2.4 \times 10^{-14} \theta^4.\]

The various coefficients have been calculated through regression data from
a number of sources, and are given as the best estimates available.

The substitution of (6.15) and (6.17) into (6.13-14) and a subtraction give now an explicit expression for the function $\beta=\beta(p,\theta)$. The barothermometric path $\beta(p,\theta)=0$ is accordingly drawn (fig. 2, curve "a") in the rectangle $[x,J]$, where $l$ goes from $p_0=0$ to $p=30$ kbar, and $J$ goes from $\theta_0=30^\circ C$ to $\theta=900^\circ C$. These pressure and temperature ranges are of interest in Mineralogy and in Earth Sciences, especially in connection with the study of metamorphic rocks and sediments.

As is perhaps clear, the results obtained through the procedure illustrated above should be considered as rather tentative. An alternative method is suggested by some of the formulas Thurston obtained in [47] before writing his equations (6.13-14), as we now explain.

In connection with $U=U(p,\theta)$, let us introduce the so-called $2^{nd}$ and $3^{rd}$ order elastic stiffnesses $\sigma$ and $\sigma'$ respectively, at atmospheric pressure (cf. (5.7)):

\begin{equation}
\sigma(\theta) = \phi_{cc}(C(p_0,\theta), \theta) \\
\sigma'(\theta) = \phi_{ccc}(C(p_0,\theta), \theta).
\end{equation}

The compliances $\kappa$ are then defined by the condition (5):

\begin{equation}
\kappa(\theta) = \sigma^{-1}(\theta).
\end{equation}

Thurston [47] gives the relations linking the elastic coefficients $\kappa$ and $\sigma'$ to the parameters appearing in (6.9) and (6.16). These relations are long and tedious and need not be explicitly noted here (see [47, eqs. (34) and (91)-(106)]): by means of them, the functions $A_1(\theta)$, $A_3(\theta)$, $B_1(\theta)$, $B_3(\theta)$, $B_0(\theta)$, $B'_0(\theta)$ can be calculated, once the temperature dependence of $\kappa$ and $\sigma'$ is estimated.

On the one hand, data are available to represent the function $\kappa(\theta)$ as a cubic polynomial expression; in Brice [51, tables XVIII, XXI, and XXV] the room temperature values of the $1^{st}$, $2^{nd}$ and $3^{rd}$ order temperature derivatives of the compliances $\kappa$ are given, so that the usual polynomial expansion about $\theta=\theta_0$ can be obtained (6).
On the other hand, there is a complete lack of data on the temperature dependence of the 3rd order stiffnesses $\sigma'$, whose value is known only for $\theta = \theta_0$. The (constant) values $\sigma'(\theta_0)$ evaluated by Thurston et al. [52] will be used here for the functions $\sigma'(\theta)$.

In this way, the following functions of $\theta$ are obtained, with $\theta_0 = 25^\circ C$ and $\theta = \theta - \theta_0$:

$$
A_1 = -9.81 \times 10^{-4} - 2825 \times 10^{-10}\theta - 4446 \times 10^{-13}\theta^2 - 6978 \times 10^{-16}\theta^3,
A_3 = -6.30 \times 10^{-7} - 1768 \times 10^{-10}\theta - 4157 \times 10^{-13}\theta^2 - 4930 \times 10^{-16}\theta^3.
$$

\[ (6.20) \]

$$
B_1 = 15.51 \times 10^{-6} + 1326 \times 10^{-11}\theta + 2599 \times 10^{-14}\theta^2 + 72 \times 10^{-17}\theta^3,
B_3 = 14.54 \times 10^{-6} + 908 \times 10^{-11}\theta + 2450 \times 10^{-14}\theta^2 + 68 \times 10^{-17}\theta^3,
B_0 = (26.42 \times 10^{-4} + 7419 \times 10^{-10}\theta + 13055 \times 10^{-13}\theta^2 + 18886 \times 10^{-16}\theta^3)^{-1}
$$

\[ B'_0 = \frac{45.77 \times 10^{-6} - 7650 \times 10^{-11}\theta + 3548 \times 10^{-14}\theta^2 - 27 \times 10^{-17}\theta^3}{7.24 \times 10^{-6} + 371 \times 10^{-11}\theta + 749 \times 10^{-14}\theta^2 + 1196 \times 10^{-17}\theta^3} \]

Again, the substitution of (6.20) and (6.17) into equations (6.13-14) and a subtraction give the function $\beta = \beta(p, \theta)$, and the relative barothermometric path $\beta(p, \theta) = 0$ is shown in Fig. 2, curve "b". The pressure and temperature ranges I and J chosen are the same as for curve "a": from $p_0 = 0$ to $p = 30$ kbar and from $\theta_0 = 25$ to $\theta = 900^\circ C$, respectively. The slight difference in the value of $\theta_0$ for curves "a" and "b", is due to the experiments being performed at different (room) temperatures in the two cases.

Remark: It is worth noting that both the curves "a" and "b" obtained above are completely inside the area corresponding to the low quartz phase in the phase diagram of $SiO_2$ as this is presented by Dana [5, vol. 3, p. 5], for instance. Thus this is the lowest phase of silica, within the pressure and temperature intervals chosen here.

Just for the sake of further comparison, let us show the result which is obtained when one does not consider at all the temperature-dependence of the material parameters appearing in formulas (6.13-14). This is equivalent to assuming that the form of the functions $\alpha(p, \theta)$ and $\beta(p, \theta)$ can be given as follows:
\[
\alpha(p, \theta) = \alpha(p_0, \theta) \alpha(p, \theta_0).
\]
\[
\alpha(p, \theta) + \beta(p, \theta) = [\alpha(p_0, \theta) + \beta(p_0, \theta)][\alpha(p, \theta_0) + \beta(p, \theta_0)],
\]

where the functions \(\alpha(p_0, \theta)\) and \(\alpha(p_0, \theta) + \beta(p_0, \theta)\) are always given by their polynomial expressions (6.17), and where \(\alpha(p, \theta_0)\) and \(\alpha(p, \theta_0) + \beta(p, \theta_0)\) can be described by inserting into (6.13-14) the room temperature values of \(A_1, A_3, B_1, B_3, B_0\) obtained from (6.20) by truncating to the constant terms the polynomials there appearing, and obtaining in this way the usual THURSTON equations for quartz (cf. [47]).

This procedure leads to the barothermometric path "c" drawn in fig. 2. It is immediately seen how much this curve departs from the two others. On the contrary, the curves "a" and "b" are in good agreement, especially within the range 0-15 kbar, which is the most interesting in the applications relating to the Earth Crust. In this way, they give support to each other, and suggest that the linear extrapolations (6.15) obtained from BRIDGMAN's data are good enough, especially if one takes into account the great differences exhibited by data collected from different samples of material, mentioned in footnote (6).

We think that both the paths "a" and "b" furnish reliable means of assessing the temperature [pressure] conditions of sites in which quartz crosses are found, when the pressure [temperature] values can otherwise be estimated.

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Footnotes.

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(1) In a hexagonal lattice, the four indices ("Bravais-Miller" indices) \([u \ v \ t \ w]\) of a given crystallographic direction (i.e. of a direction containing a one-dimensional sub-lattice) \(D\) are obtained by introducing a fourth axis \(E_4=-(E_1+E_2)\) and resolving \(D\) into 4 components

\[
D = u \ E_1 + v \ E_2 + t \ E_3 + w \ E_4,
\]

with the condition \(v + w + t = 0\) (see for instance OTTE and CROCKER [53]). This notation is useful in many crystallographic computations and is widely used. Since the index \(t = -(u + v)\) is of course redundant, it can be omitted, so that the row \([u \ v \ t \ w]\) is often indicated as \([u \ v \ w]\).

(2) Crystallographic (or rational or lattice-) planes are planes containing two dimensional sub-lattices ("nets") of a given lattice. They are characterized by integral indices, that is, their normal directions can be expressed as integral combinations of the reciprocal lattice vectors \(E^a\). Two rational planes of a lattice are said to be crystallographically equivalent when they can be brought into coincidence by a point group operation, so that they have the same indices relative to suitable congruent sets of lattice vectors.

(3) The assumption that \(R\) be a natural state for \(p = p_0, \theta = \theta_0\), should probably be made more precise by saying that the configuration observed at room pressure and temperature is actually (undetectably) close to a stress-free stable equilibrium state, since residual stresses and energies are usually present at such twin boundaries. This goes together with the assumption that the twinning operation \(R_0\) at room pressure and temperature be exactly a \(90^\circ\) rotation (see sect. 2). Since the twinning operation is sensitive to environmental changes, as will be shown in sect. 4, it seems likely that, for \(p = p_0, \theta = \theta_0, R_0\) could be very close to a \(90^\circ\) rotation, rather than exactly so. Furthermore, the composition plane \(\Sigma_0\) is assumed here to have indices that depend on the ratio \(c_0/a_0\) of the room temperature and pressure values of the lattice parameters (see (2.3) and (1.3)). Of course this just means that the interface is actually a plane.
which almost coincides with the plane $\mathcal{A}_0$ indicated here, and whose actual indices, which do not depend on $a_0$ or $c_0$, have values almost coinciding with the ones indicated by (2.3).

The assumption about the reference configuration $R$ that best suits the experimental data should hence be that $R$ is very close to a natural state of the polycrystal, which is in turn to be found within a "small" neighborhood of the point $(p_0, \theta_0)$, rather than exactly there.

(4) The Born hypothesis cited in the text seems quite obvious when stated in connection with the relatively "small" macroscopic deformations that a crystal undergoes in compression or in thermal expansion as a consequence of the changes of the environmental conditions, so obvious that in most of the experimental literature it is taken for granted without further comment. In spite of this, it is by no means obvious that such an easy connection exists between the macroscopic and atomic descriptions in general, that is, for "larger" deformations. Indeed in some cases the Born hypothesis as stated in sect. 6 can be proved false: such is the case for instance of the shear deformations involved in many of the mechanical twinning modes common for the hexagonal metals (see for instance RAPPENPORT [54]). Nevertheless, experimental evidence indicates that, in the case of single lattice structures, the Born hypothesis does hold even in the range of large twinning deformations, a clear example being given by crystalline mercury (see CROCKER et al. [55], GUYONCOURT and CROCKER [56]).

(5) The stiffness tensor $\sigma$ is meant here as a linear transformation of the space of all symmetric (second order) tensors into itself.

(6) The values tabulated in BRICE [51] for the various derivatives of the elastic compliances are from different sources, and individual sets of data show considerable divergence. As recommended in [51], the ones used here are from BECHMANN et al. [57], reappraised by various authors.

It is worth noting that the above mentioned measures of temperature derivatives refer to the adiabatic elastic coefficients, whereas the iso-thermal ones, defined by (6.18-19), are of interest here. Nevertheless, the distinction is immaterial: in fact, the differences about the data referring to various different samples of material are always found to be very large, probably owing to the different grades of purity of the crystals. For
instance, the sets of data obtained for the adiabatic compliances and their
temperature derivatives in different specimens differ much more than the
isothermal or the adiabatic coefficients differ from each other. This can be
seen by comparing for instance the values in SKIMIN et al. [58, table
XIV, columns 1 and 2] and in BRICE [51, tables XXI, XXII column 2, XXVI].
However, the (constant) room temperature values (i.e. the first terms in
the cubic polynomial expansion of the compliances \( \kappa \) about \( \theta = \theta_0 \)) differ by
significant amounts in the isothermal and in the adiabatic cases, and since
they are available, the isothermal values given in [58, table XIV, column 2]
are used here.
Fig. 1 The reference configuration $R$ of the quartz cross, at normal conditions. The three "arms" $R_1, R_2, R_3$ are obtained from the arm $R_0$ through the rotations $R_0, R_0^2$ and $R_0^3$ respectively, $R_0$ being the $90^\circ$ rotation described in Sect. 2.
Fig. 2 The barothermometric path $\beta(p,\theta)=0$ obtained by means of the temperature-correction of the THURSTON equations described in Sect. 5.
Curve "a" refers to the data in [34].
Curve "b" refers to the data in [51], [52], [57] - [60].
Curve "c" does not employ the temperature-correction.
References


[38] B. Olinger, P. M. Halleck, "The compression of $\alpha$-Quartz", J. Geophys. Res. 81, 5711, 1976.


