The role of the incommensurate phase in the opalescence of quartz

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Abstract

Forty five years ago, an intense light scattering was observed at the α–β transition of quartz but the origin of this opalescence has remained mysterious for a long time. Recently Saint-Grégoire *et al* and Aslanyan *et al* have explained the origin of the opalescence by introducing new incommensurate ('inc') phases with ferroelastic properties in the transition region. In this paper we recall the main features of the α–β transition, of the inc phase and of the opalescence of quartz, which presents different properties in two regions of the α–inc phase boundary. We also describe the three typical structures observed in the phase boundary regions by electron microscopy. We present briefly the two previous ferroelastic models and we propose our own explanation for the origin of the opalescence. We discuss the relations of these three models with experimental results concerning thermal behaviour, microscopic structures and the origin of the refractive index variations. Most experimental results are in agreement, at least qualitatively, with our model where the two opalescence regions correspond respectively to the presence of inc rotation patches and of irregular Dauphiné microtwins, both in a non-equilibrium state.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the last 40 years, the field of structural phase transitions [1] has been greatly enriched by the discovery of several new phenomena: soft modes and incommensurate (inc) structure [2]. One of the oldest known examples of a structural phase transition, the α–β transition of quartz, has been a subject of continuous interest since its discovery by Le Chatelier in 1889 [3]. In a historical review, Dolino [4] has presented several outstanding precursor results obtained on this material: the relation between the crystalline structures of the two phases [5], the first observation of a soft mode [6], the behaviour of the order parameter at

a discontinuous transition [7] and finally the discovery of the inc phase of quartz [8]. A remarkable phenomenon observed in this material is the transition opalescence, which is a very intense light scattering (LS) occurring just at the α–β transition, discovered in 1956 by Yakovlev *et al* [9]. The origin of this phenomenon remains one of the most puzzling questions in quartz research. Recently Saint-Grégoire *et al* [10] and Aslanyan *et al* [11] independently developed detailed models explaining the origin of the quartz opalescence by the existence of new and very different ferroelastic inc phases, which has led to ongoing controversy between the two groups [12, 13].

The aim of the present paper is to give a critical account of this complex phenomenon and to present a new interpretation of the quartz opalescence. Due to the present controversy on the origin of the quartz opalescence, we first recall, in part 2, the main experimental results concerning the α–β transition, the inc phase and the transition opalescence. We also describe the microscopic structure of the phase boundary disclosed by various electron microscopy experiments. In part 3, we present the two models with ferroelastic phases [10, 11] and we develop our own interpretation of the quartz opalescence. In part 4, we discuss the relations between the three models and the experimental results concerning thermal conditions, relations between macroscopic and microscopic observations and the variations of the refractive index producing the opalescence. Finally we suggest some new experiments to test the validity of the various models and we present our conclusions.

2. Previous results on the α–β transition and on the opalescence of quartz

2.1. Physical properties of quartz and the α–β transition

As the properties of quartz are well described in many textbooks, we only recall some results useful to understand the origin of the opalescence, already reviewed by Yakovlev and Shustin in 1983 [14]; further information on quartz is found in a recent review on silica materials [15]. Results on the α–β transition and on the inc phase of quartz, with short mentions of the quartz opalescence, are given in review papers of Dolino *et al* [16].

Quartz is the stable phase of SiO_2 at ambient conditions. It is a clear transparent crystal with uniaxial birefringence and optical rotatory power along the Z-axis. At room temperature, α-quartz is a trigonal crystal with a structure built from nearly regular SiO_4 tetrahedra, interconnected by common oxygen corners. Upon heating, there is a discontinuous transition at $T_h = 847$ K, to the β-phase with a higher hexagonal symmetry. Both phases have three SiO_2 groups in the unit cell. The change of symmetry is due to small displacements of the atoms, which, in a first approximation, correspond to a rotation of rigid SiO_4 tetrahedra around the X-axis by an angle η, which is the order parameter of the α-phase. The two possible signs of η correspond to the existence of domains, called Dauphiné twins (from the name of the region around Grenoble, where such twinned samples have been frequently found). Upon heating, η decreases continuously from $16°$ at room temperature to $6°$ at T_h, where there is a final discontinuous jump to $\eta = 0$, the constant value in the β-phase. These variations are in good agreement with the predictions of Landau theory, for discontinuous first-order transitions [7]. Upon cooling, the transition to the α-phase occurs with a thermal hysteresis of about 1 K, at $T_c = T_h - 1$ K. Although the optical properties of quartz have been studied for a long time, Bachheimer in 1980 [17] observed, upon cooling, a previously unnoticed increase of the birefringence starting at $T_i = T_c + 1.4$ K. This variation, plotted in figure 1, corresponds to the existence, between T_i and T_c, of the inc phase described in the next section.
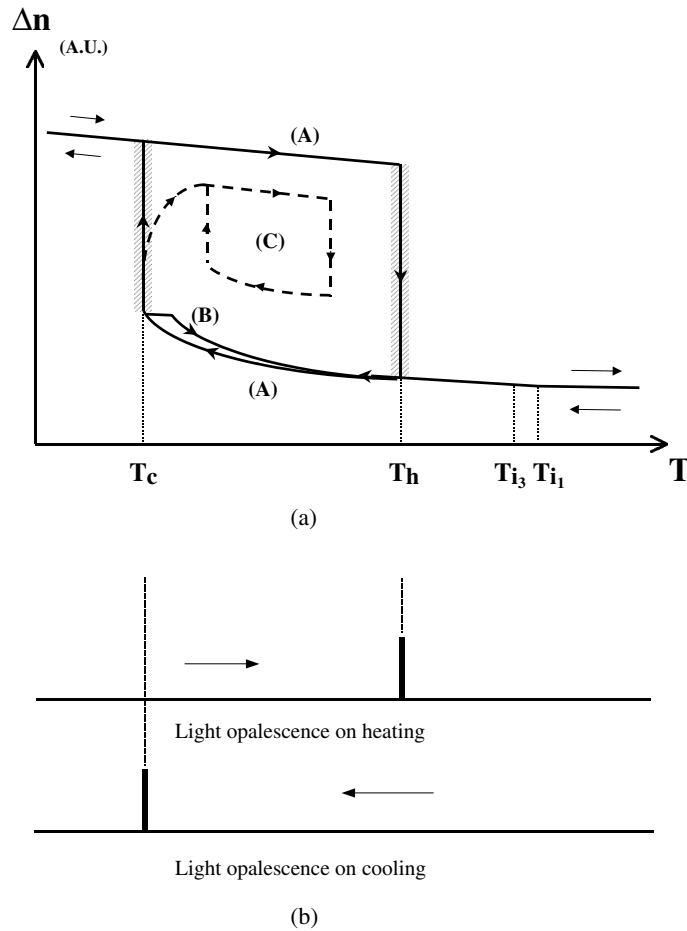
Figure 1. (a) The schematic variation of the birefringence in the α–inc–β transition region of quartz, showing the transition hysteresis and the presence of two inc phases ($3q$ and $1q$) between T_{i1}, T_{i3} and T_c. Curve (A): the heating and cooling temperature cycle between α- and β-phases [17]. Curve (B): global hysteresis of the $3q$ inc phase [25]. Curve (C): the temperature scan obtained after stabilization of the coexistence state between the α-phase and the $3q$ inc phase in a temperature gradient [38]. (b) The opalescence is observed at T_h upon heating and at T_c upon cooling, in a temperature cycle corresponding to the birefringence curve (A).

2.2. Properties of the inc phase

In 1978, Aslanyan and Levanyuk [18] suggested, in a theoretical work, that an inc phase could exist between the classical α- and β-phases of quartz: this is due to the presence, in the Landau free energy, of a coupling between elastic strains u_{ij} and the spatial gradient of the order parameter η, given by

$$\Delta F = (u_{xx} - u_{yy})\partial \eta/\partial x - 2u_{xy}\,\partial \eta/\partial y. \tag{1}$$

This remarkable proposition has been fully confirmed by the observation of satellite peaks in diffraction experiments using neutrons [8,19], x-rays [20] and electrons [21], in a temperature range of 1.4 K, between T_i and T_c. In fact the most accurate measurements [22] disclosed the existence of two inc phases: in a 0.05 K temperature range between T_{i1} and T_{i3}, there

is a $1q$ phase, of orthorhombic symmetry, with a single modulation wavevector q_i, exactly parallel to one of the three unit vectors b^* of the reciprocal space in the plane perpendicular to the Z-axis. The main $3q$ phase, existing between T_{i3} and T_c, has a $3q$ structure produced by the superposition of three modulation waves at $120°$. The modulus of the wavevectors q_i decreases from $0.032\ b^*$ at T_{i3} to $0.022\ b^*$ at T_c [23]. A specific feature of the $3q$ phase is that the vectors q_i are rotated away from the b^*-directions by a small angle $\pm\phi$ increasing from $1°$ at T_{i3} to $6°$ at T_c [24]. Orientation domains corresponding to the two opposite values of ϕ are observed [24]. A global hysteresis is observed in the temperature variations of the modulation waves and of most physical properties, as shown by curve (B) of figure 1 for the birefringence [25]. In fact the coupling term ΔF of equation (1) corresponds to an interaction between the soft mode of the α–β transition and an acoustic mode [18, 26], which has indeed been observed in subsequent inelastic neutron scattering measurements in the β-phase [27]. The presence of an inc phase leads to the existence of new vibration modes (amplitudons and phasons). However, in quartz, these modes are overdamped and only a broad quasielastic scattering is observed [28–30]. A weak LS is also produced by the boundaries of the rotation domains of the inc phase [31, 32].

2.3. Previous experiments on the opalescence of quartz

In 1956, Yakovlev *et al* [9] discovered an intense LS phenomenon, occurring at the α–β transition of quartz, in a 'fog zone' of a few mm thickness. By analogy with the critical opalescence of fluids, they attributed the existence of this LS to the effect of thermodynamic fluctuations. Independently, in 1955, Ginzburg [33], using the Landau theory of the second-order transition, proposed that order parameter fluctuations can produce a strong LS and he mentioned a possible application to the quartz transition. After the observation of the quartz opalescence, Ginzburg and Levanyuk [34] developed further the fluctuation model of LS. Ginzburg [35] also proposed a relation between this LS and the recently introduced concept of a soft mode, but without reference to the first observation of a soft mode in any materials, achieved in 1940 by Raman and Nedungadi in quartz [6].

Around 1968, to observe the predicted relation of the opalescence with a soft mode, Shapiro *et al* [36] performed new LS measurements at the quartz transition with laser instrumentation: they observed a static speckle in quartz opalescence, which is incompatible with fluctuation models. Furthermore, they observed that the opalescence appeared only in a small temperature range of a few hundredth of a degree, during the coexistence of the two phases, with a thermal hysteresis of 1 K between heating and cooling: this was definitive proof of the first-order character of the quartz transition.

In 1977, using a small temperature gradient to stabilize the phase coexistence, Dolino and Bachheimer [37] discovered a second LS phenomenon at the quartz transition: an intense small-angle scattering (SAS) of light is observed in a region adjacent to the fog zone. They also discovered the striking anisotropy of the two LS phenomena, which are observed only for scattering wavevectors perpendicular to the Z-axis. Figure 2 shows an optical microscopy picture of the two LS regions obtained upon cooling. On the high-temperature side, there is the SAS region, produced by cylindrical objects parallel to the Z-axis with diameters of a few tens of μm. On the low-temperature side there is the large-angle scattering (LAS) region, corresponding to the fog zone of Yakovlev *et al* [9]: this is also an anisotropic LS, produced by cylinders parallel to the Z-axis, but with diameters in the μm range. In general, the boundary (B) between the SAS and LAS regions is well contrasted, while the boundary (B′) between the LAS region and the α-phase has a weaker contrast; there is no distinct boundary between the SAS region and the high-temperature phase, which in fact is the $3q$ inc phase.
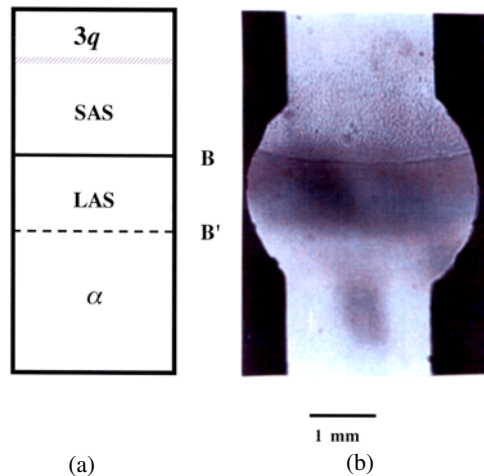
Figure 2. (a) A schematic drawing of the two LS regions, SAS (producing the small angle scattering of light) and LAS (producing the large-angle scattering of light), present in a quartz sample, between the $3q$ inc phase and the α-phase during the coexistence state. (b) A photographic image of the corresponding regions observed upon cooling, obtained with a light beam along the Z-axis.

Table 1. Recapitulation of the various regions present between the α-phase and the $3q$ inc phase during quartz opalescence, where SAS and LAS of light were observed. The structure at the origin of the LS is indicated as given at the time of publication. The last three lines correspond to the three models discussed in this work.

Authors	Year	Reference	LAS (fog zone)	SAS (m-zone)
Yakovlev *et al*	(1956)	[9]	Fluctuations	
Shapiro *et al*	(1968)	[36]	Twins	
Dolino and Bachheimer	(1977)	[37]	Twins	α–β mixing
Shustin *et al*	(1978)	[14, 39]	Defects	Defects
Shigenari *et al*	(1980)	[40]	II	I
Saint-Grégoire *et al* [a]	(1996)	[10]	α–inc interface[a]	inc ELT
Aslanyan *et al*	(1998)	[11]	$b^*/3$	inc $b^*/3 + \kappa$
Dolino and Bastie	(2001)	This work	Twins	inc EQT

[a] The model for the LAS region was introduced later by Saint-Grégoire [51].

Similar results on the two anisotropic LS regions were obtained in other studies performed around 1980 by Dolino [38], Shustin *et al* [39] and Shigenari *et al* [40]. These results have been reviewed by Yakovlev and Shustin [14]. Shigenari *et al* [41] have performed the only recent measurements of the quartz opalescence. A summary of the previous experimental results is given in table 1. One can note the good agreement between the various observations of the two spatially distinct LS regions (SAS and LAS), although there are some differences in the reported temperature behaviours, which are discussed in section 4.1.

2.4. Electron microscopy observations of the boundary between α- and inc phases

Previous optical measurements have shown that the opalescence of quartz is due to two adjacent inhomogeneous regions occurring between the α- and the $3q$ inc phases. Detailed information on the structure of the interphase boundary has been obtained by transmission electron microscopy (TEM). The first measurements of the phase boundary region, by Malov and Sonyushkin [42] and by Van Tendeloo *et al* [43], showed periodic patterns of black and white equilateral triangles (EQTs) in the (001) plane. These pictures were first interpreted as an extensive Dauphiné microtwinning, producing the transition opalescence in the fog zone of Yakovlev *et al* [9]. However, after the discovery of the inc phase, it was clear that the
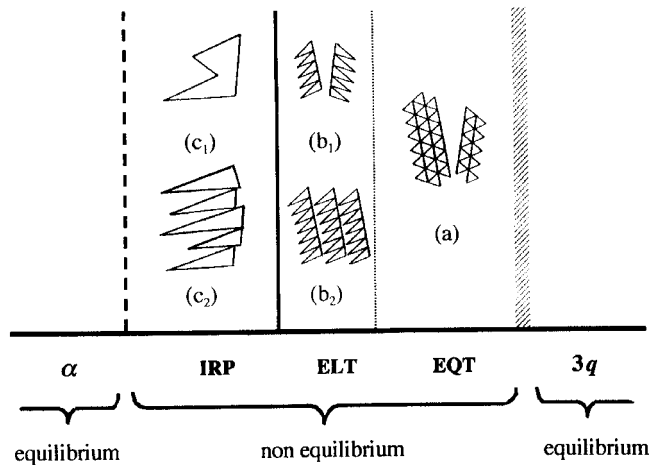
Figure 3. Schematic representations of the three typical structures observed in electron microscopy experiments between the $3q$ inc phase and the α-phase of quartz: EQT: equilateral triangles; ELT: elongated triangles; IRP: irregular polygons. Pictures (a), (b$_1$) and (c$_1$) were obtained from the results of Van Landuyt *et al* [45] and Yamamoto *et al* [46], (b$_2$) from Saint-Grégoire *et al* [10] and (c$_2$) from Snoeck and Roucau [47].

triangular patterns were a direct picture of the $3q$ inc phase, as was indeed confirmed by new TEM experiments [44]. The three typical patterns, observed by TEM in the phase boundary region [45–47], which are schematically represented in figure 3, are discussed below.

(a) Equilateral triangle (EQT) patches. All TEM experiments show the characteristic triangular pattern of the rotation domains of the $3q$ inc phase. In going toward the α-phase side, the size and the rotation of the triangles increase, producing well contrasted discontinuous EQT patches, shown in figure 3(a). A quantitative analysis of these pattern is given in table 2. The maximum values of the EQT wall distance d and of the rotation angle ϕ, measured on the TEM pictures, are larger than the equilibrium values, measured at T_c, just before the nucleation of the α-phase, by diffraction experiments on macroscopic samples [20, 23]. Although a qualitative change of the EQT contrast has been mentioned by Yamamoto *et al* [46] around the equilibrium values at T_c ($d = 20$ nm and $\phi = 6°$), it seems that the important consequences of the non-equilibrium nature of the rotation patches have not been fully appreciated before. The large value of d, measured during the coexistence with the α-phase, is confirmed by the results of diffraction measurements [20, 44, 48], performed on macroscopic samples, in the coexistence state. Unfortunately, due to a limited resolution, the rotation angles were not determined in these measurements.

(b) Elongated triangles (ELTs). The systematic presence of more or less periodic ELT structure has often been observed: these triangles combine three allowed wall orientations, giving triangle angles of 2ϕ, $60°$ and $120° - 2\phi$. The maximum value of ϕ is around $10°$ and the size of the smaller triangle side is in the 100 nm range [45]. As shown in figure 3(b$_1$), the ELTs are often observed with linear periodic arrangement along well defined directions, which, as mentioned by Van Landuyt *et al* [45] '*suggests the existence of an incipient inc structure with a lower symmetry*'. Small patterns of two-dimensional periodic elongated triangles (2D-ELT) were indeed observed by Snoeck *et al* [21, 47] and Yamamoto *et al* [46]. The larger and

Table 2. Values of the rotation angles ϕ and of the wall distance d of the $3q$ inc phase. (a) The maximum value in the equilibrium state just above T_c; (b) the maximum value at the lower temperature of the coexistence state. Asterisks indicate cases where the rotation angles were not resolved.

	(a) Equilibrium		(b) Coexistence state						
	X-ray	Neutron	X-ray	Neutron	γ-ray	TEM			
Angle ϕ(°)	7	6	*	*	*	10	10	10	11
Wall distance d (nm)	23	19	56	40	80	45	50	62	45
Reference	[24]	[23]	[20]	[44]	[48]	[21]	[44]	[45]	[46]

more periodic 2D-ELT pattern, observed by Saint-Grégoire *et al* [10, 49], is represented in figure 3(b₂).

(c) Irregular polygons (IRPs). Finally on the α-phase side, irregular polygonal or triangular objects, represented in figure 3(c₁), have been observed in most TEM experiments. Studies of the contrast variation of different reflections [44, 46] show that they have an atomic structure similar to that of Dauphiné twins. However, their elongated triangular shapes and their small size, in the micrometre range, distinguish them from the usual Dauphiné twins, remaining at lower temperature. Memory effects on the shape and position of pre-existing twins are often observed in the α-phase after a short annealing in the β-phase [50]. Just at the α-phase boundary, Snoeck and Roucau [47] have observed a new feature (shown in figure 3(c₂)) of irregular parallel triangles. A similar picture, also obtained by Snoeck, was published in the most recent paper of Saint-Grégoire [51], as support for his LAS model. The nature of these structures is discussed in section 4.2. Lower-resolution pictures of Dauphiné twinning and of the phase boundary have also been obtained by x-ray topography in Japan [24, 52].

To explain the origin of the opalescence, it is necessary to understand the nature of the three intermediate regions observed by TEM and, with the hypothesis that they are present in macroscopic samples, to find their relations with the two LAS and SAS regions: this is clearly a delicate problem.

3. Models for the origin of the opalescence

3.1. Initial models

When Yakovlev and Shustin [14] published their review, in 1983, on the quartz opalescence, the main experimental features, summarized in table 1, were already well known, but the origin of these LS phenomena remained rather mysterious, as the recent discovery of the inc phase was not considered. The initial fluctuation models [9, 33, 34], in contradiction with the static speckle of the opalescence observed by Shapiro *et al* [36], were already discredited and two other models have been proposed:

- The heterophase model, which is a fine mixing of α- and β-phases, tentatively introduced by Semenchenko [53] to explain the thermodynamic properties of the quartz transition, has been used by Bartis [54] to explain the quartz opalescence.
- The Dauphiné microtwins model, introduced by Young [55] to interpret his x-ray results, was developed by Shapiro *et al* [36] to explain their LS measurements. At this time, this model was apparently supported by the initial interpretation of the TEM results [43].

Dolino and Bachheimer [37, 38] used these two models to explain the origin of the two LS phenomena observed in quartz: SAS and LAS would be produced respectively by the heterophase structure and by Dauphiné microtwinning. The hypothesis for the SAS region was criticized by Yakovlev and Shustin [14]: they claimed that in the heterophase model, the variation of the refractive indices of the SAS objects would be much larger than their estimation of 1×10^{-5}.

After the discovery of the inc phase, Dolino *et al* [44] considered that the explanation of the LAS by Dauphiné twins was still valid but that the heterophase model was clearly obsolete (however, as exhibited in figures 1 and 2, the LS phenomenon occurred only during the coexistence of macroscopic regions of α- and inc phases in the sample). The SAS was then attributed to the EQT rotation patches observed in the same paper [44]. This is still the starting point of our model, developed below.

3.2. Inc ferroelastic phase models of the quartz opalescence

Recently, Saint-Grégoire *et al* [10] and Aslanyan *et al* [11] introduced two new models, where the quartz opalescence is explained by the existence of new inc ferroelastic phases, stable in a finite temperature range above T_c. However, they proposed very different microscopic structures for these new phases, which has led to further controversy between the two groups [12, 13]. We now briefly introduce these two ferroelastic models; our criticisms are developed, in section 4, in relation to experimental results

Using the classical theory of the inc phase of quartz [18], Saint-Grégoire *et al* [10] developed a model based on their TEM observations of the 2D-ELT structure reported in the same paper. By evaluating the competition between the energy of distant parallel walls and the energy of wall crossing, they predicted the existence, just above T_c, of a stable ferroelastic ELT phase. According to their TEM measurements, this phase would be present in a small temperature range of 0.1 K. Finally they explained, but without quantitative evaluation, that the modulation of the refractive indices of the ELT ferroelastic domains would produce the SAS. To explain the origin of the LAS, Saint-Grégoire [51] has recently complemented the initial model by proposing the existence of a supplementary interfacial structure, corresponding to the irregular parallel triangles observed by Snoeck and Roucau [47], represented in figure 3(c_2).

The model of Aslanyan *et al* [11] represents a major departure from the classical model, previously used with great success to explain the existence and the properties of the inc phase of quartz [18, 26]. They also proposed that the intense opalescence of quartz is due to the domains of a ferroelastic inc phase, but with a drastically different structure. Using the usual quadratic expansion of the physical properties of inc phases as a function of the modulation wavevector q, they estimated the variation of the refractive index of the inc ELT ferroelastic phase of Saint-Grégoire *et al* [10]. For the usual inc modulation around the Brillouin zone centre with $q = 0.01\ b^*$, they found $\delta n \sim 10^{-8}$, too small to produce the intense opalescence. On the basis of this theoretical estimation, they conjectured that the inc modulation of quartz does not occur near the centre of the Brillouin zone, as previously observed, but around $b^*/3$. Then with a large wavevector $q = b^*/3 + \kappa$, the quadratic expansion gives a variation of the refractive index larger by three orders of magnitude, which can easily produce the quartz opalescence. To explain why satellite peaks around $b^*/3$ have never been observed, they used their recent theory of the Debye–Waller factor of inc phases [56]. In the inc phase of quartz, a complete extinction of the first- and second-order satellites is predicted; only the third-order satellites, enhanced by a coupling with strain, would be observed, again with a small wavevector 3κ. The SAS would be produced by the ferroelastic domains of this new inc phase. Finally, the LAS is attributed to the orthorhombic ferroelastic domains of the commensurate phase, produced by the lock-in of the modulation wave at $b^*/3$.

3.3. Our model: EQT patches and irregular Dauphiné microtwins in a non-equilibrium state

The starting point of our model is the previous proposition of Dolino *et al* [44], that SAS is due to the EQT rotation patches. However, this model is greatly improved in the present work by the introduction of the non-equilibrium character of the EQT patches, disclosed in table 2. The fundamental difference of our model from the two previous ones is that we take into account the experimental fact that the opalescence occurs only during the coexistence of α- and inc phases, which induces large coherence stresses modifying the properties of the two adjacent phases. In the equilibrium state, the usual theory of inc phases [2] predicts a relation between the increase of the modulation period and of the order parameter, for temperature decreasing toward the lock-in temperature T_c. We suppose that in the coexistence state, the modulated order parameter also follows the discontinuous increase of the modulation periods, observed in the TEM pictures of the EQT patches. This leads to an inhomogeneous increase of the refractive indices in the rotation patches producing the SAS. In fact the major hypothesis of our model is that the EQT patches, observed in TEM, are also present in the phase boundary region of macroscopic samples, but with a larger size in order to produce the SAS. A similar increase of scale is needed in all the models based on TEM, as it is necessary to pass from the submicron size of the TEM patterns to the tens of microns size corresponding to the SAS objects.

For the LAS, we still use the old hypothesis that it is produced by the Dauphiné microtwins, observed in TEM experiments. However, as at equilibrium the two Dauphiné twin variants have the same refractive indices, it is necessary to introduce a mechanism producing a variation of the refractive indices in the twin region. The first explanation, introduced by Shapiro *et al* [36], was a variation of the refractive indices in twin walls. Our initial proposition [37,38] was based on the photoelastic effect induced by the coherence stresses, which however are difficult to evaluate. A more likely possibility is the non-equilibrium character of the Dauphiné twins in the vicinity of the phase boundary, which then can have different absolute value of the order parameter. Another explanation is that the transition occurs under a bias field, linearly coupled to the order parameter η, as suggested by the observation of twin memory [50]. The presence of this bias field increases the value of η in the favoured twin orientation and decreases its value in the unfavourable orientation. Probably all these effects contribute to a greater or lesser extent to the variation of the refractive indices in these Dauphiné microtwins, which is at the origin of the LAS.

4. Discussion of the three models of the quartz opalescence

As the origin of the quartz opalescence is explained in very different and even controversial ways by the three models, we now discuss the predictions of these models in relation to experimental results, concerning temperature behaviour, microscopic structure and optical properties.

4.1. Thermal conditions

As there is often some confusion in experiments on quartz transitions, resulting from the combined effects of a temperature gradient and of the 1 K hysteresis of the first-order α–inc phase transition, we have plotted in figure 4 the phase diagrams corresponding to the three models. Figure 4(a_1) exhibits the phase diagram obtained upon cooling, from our diffraction [22, 48, 57] and optical [58] measurements of the inc phase, complemented by our older studies of the transition opalescence [37, 38]. In these measurements, there is absolutely no indication of the existence of a new phase, stable above T_c. But even in the best conditions, there is always a temperature gradient on a quartz sample of finite size, which
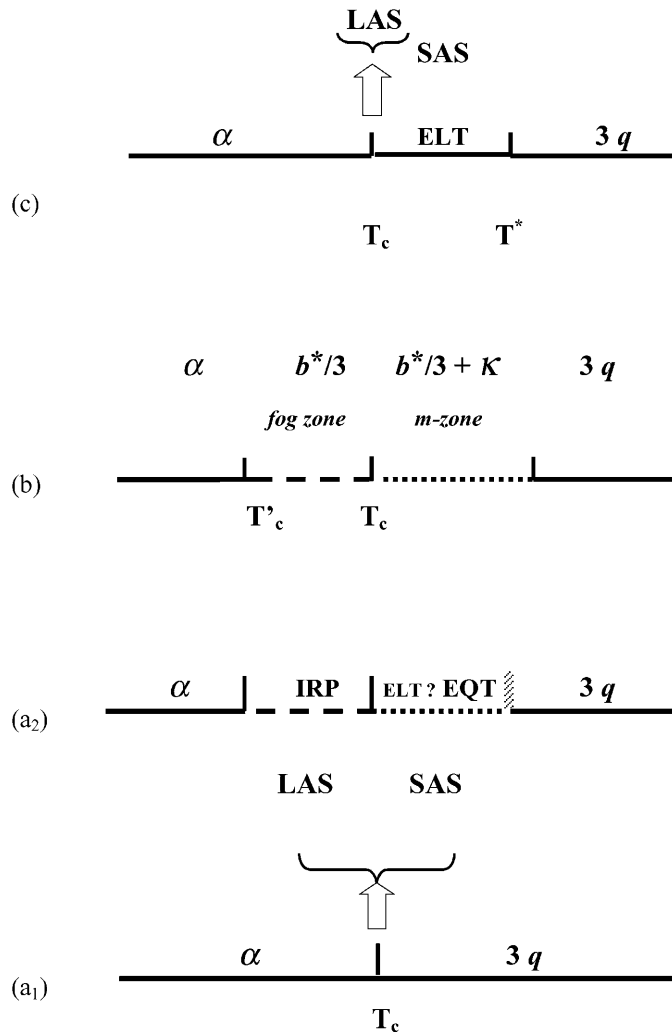
Figure 4. Phase diagrams corresponding to the three models discussed in this work, with indications of the various regions observed in LS and electron microscopy experiments. (a) Phase diagrams corresponding to our model. (a$_1$) This phase diagram is based on measurements performed during a cooling scan, started in the homogeneous $3q$ phase; the SAS and LAS opalescence are observed only during the transient coexistence state. (a$_2$) The coexistence state stabilized in a temperature gradient, showing the succession of the SAS and LAS regions as a function of the temperature variation. (b) Model of Aslanyan *et al* [11] with an inc phase around $b^*/3$. Their two LS regions (m-zone and fog zone) are present in temperature ranges of 0.3 and 0.2 K around T_c, according to the measurements of Shigenari *et al* [41] performed on a sample probably stabilized in a temperature gradient. (c) The model of Saint-Grégoire *et al* [10, 51] deduced from their electron microscopy observations, with an ELT inc ferroelastic phase, stable in a temperature range of 0.1 K above T_c, producing the SAS. The LAS region is present just at T_c, after nucleation of the α-phase.

perturbs the behaviour of the first-order α–inc transition. In general, upon cooling, there is a single nucleation at T_c of the α-phase on the colder sample boundary [38]. When the temperature gradient is small, the phase boundary sweeps the sample irreversibly until the transition is completed; in this case, corresponding to curve (A) of figure 1, the two moving opalescence regions (SAS and LAS) are observed as a function of time during the transient

coexistence of α- and inc phases, at a nearly constant temperature. However, if after the nucleation of the α-phase, the temperature is increased quickly by about 0.5 K, the phase boundary can be stabilized in the middle of the sample. This stabilization of the coexistence state occurs spontaneously in the sample, in the presence of a large temperature gradient. In a stabilized coexistence state, a small temperature cycle produces a hysteresis cycle, shown by curve (C) in figure 1, and the opalescence can be observed as a function of a temperature variation [38], as schematically represented in figure 4(a_2).

In their theoretical works, Aslanyan *et al* [11, 13] gave no indication of the temperature range of the two ferroelastic phases. However, in recent measurements of LS and optical depolarization, Shigenari *et al* [41,59] have observed a fog zone and an m-zone (corresponding to our LAS and SAS regions) in two successive temperature ranges of 0.3 and 0.2 K, as shown in figure 4(b). Their results are consistent with our results of figure 4(a_1) and 4(a_2) only if their measurements have been performed on a coexistence state stabilized in a temperature gradient. In this case, the phase diagrams of figure 4(a_1) and 4(b) are not discordant: they only correspond to measurements performed in different conditions—respectively with a transient or a stabilized coexistence state. In fact the true thermodynamic equilibrium temperature is somewhere between T_h and T_c, inside the hysteresis cycle.

On the other hand, TEM measurements are performed in very special conditions: usually one observes a region, with a thickness of a few tenths of μm, at the edge of a hole, in a sample of a few mm diameter. There is always a temperature gradient due to heating of the observed region by the electron beam [21, 44]. Then during a study of the quartz transition the larger part of the sample is in the α-phase, while only the region under observation, heated by the electron beam, is in the inc or in the β-phase, a situation which is very convenient for a study of the structure of the inc–α phase boundary, although only the nucleation of the inc phase in the α-phase upon heating can be observed (on the other hand, measurements on macroscopic samples are most often performed upon cooling, to observe the maximum range of the $3q$ inc phase). In TEM measurements, the determination of the temperature is always difficult: in their accurate study of the inc phase performed with a 1 MeV electron microscope, Yamamoto *et al* [46] used a temperature scale obtained by comparison of their TEM results with those from x-ray measurements [24]. Using improved (but unspecified) temperature control, Saint-Grégoire *et al* [10], estimated that the ELT phase is stable in a temperature range of 0.1 K above T_c. In his most recent contribution, Saint-Grégoire [51] gives a schematic representation of the spatial dependence of the transition region, where the LAS is '*due to the zigzagging interface between ELT and α-phases*'. To represent the temperature dependence, he gives, in the same picture, a reproduction of our experimental LS results, measured in a temperature gradient and corresponding to figure 4(a_2). We obviously appreciate this interpretation of the LAS, using our results. However, a disturbing feature is that in his drawing the SAS region, which according to his model corresponds to the ELT phase stable in a range of 0.1 K, extends a little in the EQT phase. Correcting this point, we think that the corresponding phase diagram is given by figure 4(c). We note that this is a kind of 'hybrid' phase diagram: while the SAS occurs in an equilibrium ELT phase, stable in a finite 0.1 K range, as in the Aslanyan *et al* model of figure 4(b), the LAS is present only in a coexistence state, as in our phase diagram of figure 4(a_1).

In conclusion, we think that the most fundamental phase diagram is plotted in figure 4(a_1): it is obtained in cooling measurements, starting with the whole sample in a homogeneous high-temperature phase. The phase diagrams of figures 4(a_2) and 4(b) are deduced from optical measurements performed respectively by Dolino [38] and by Shigenari *et al* [41, 59], on a coexistence state stabilized by a temperature gradient. The phase diagram of figure 4(c), corresponding to the TEM results of Saint-Grégoire *et al* [10, 51], is probably due to the temperature gradient, systematically present in TEM measurements.

4.2. Relations between the two opalescence regions and TEM observations

4.2.1. Our model. In our view, as recalled in figure 4(a), the SAS and LAS regions correspond respectively to EQT rotation patches and to IRP Dauphiné microtwins, both in a non-equilibrium state. Our main hypothesis (also necessary in the other models) is that at least two of the three structures observed in TEM are present in macroscopic samples. In our model the transition to the α-phase occurs between the SAS and the LAS regions, in agreement with the well defined B line observed in figure 2. On the α-phase side, the weak B′ line marks the limit of the IRP Dauphiné twin zone. On the other hand, no distinct boundary is observed on the high-temperature side of the SAS region, as expected for a continuous transition between the equilibrium rotation domains of the $3q$ inc phase to the non-equilibrium EQT rotation patches. We now give some indications of the sizes of the scattering objects. In medium-quality synthetic quartz samples, x-ray topography measurements [20, 57] give a size of the $3q$ rotation domains in the hundred μm range, which is probably also the size of the EQT patches, producing the SAS (this is two orders of magnitude larger than in TEM observations). On the other hand, the LAS is due to IRP microtwins, with a size in the submicron range; this is indeed the size of IRPs observed in TEM, a little larger than the typical size, around 0.1 μm, of the elementary ELT motif.

In our model the role of the ELT region, which has not been observed in macroscopic samples, is not clear. We remark that an EQT patch, which in our model is the basic SAS object, is an assembly of small EQTs forming a large rotation domain. On the other hand, the LAS is due to IRPs, formed by individual irregular triangles, which are the final evolution stage of the elementary component of the $3q$ inc phase. According to the TEM results of Saint-Grégoire *et al* [10], the transition from the $3q$ inc phase to the α-phase is produced by two successive morphological instabilities: first, in going from EQTs to periodic ELTs, the trigonal symmetry disappears; then the spatial periodicity disappears between ELTs and IRPs. If this situation occurs in macroscopic samples, the LS effect of the periodic ELT structure is probably similar to that of the EQT, both contributing to the SAS. The ending of the spatial order corresponds quite naturally to the disappearance of the inc phase and to the boundary of the α-phase; the inhomogeneous structure present in the α-phase is basically some kind of Dauphiné twin. If there is no ELT region in macroscopic samples, there is an obvious correspondence of SAS and LAS respectively with inc EQT patches and IRP Dauphiné microtwins.

4.2.2. The Aslanyan et al model. In the description of their model [11], Aslanyan *et al* mentioned the TEM observation of Yamamoto *et al* [46], showing mostly irregular IRPs. However, they emphasize the presence of a few periodic ELTs as evidence for an inc ferroelastic phase. Although less periodic than the 2D-ELTs of Saint-Grégoire *et al* [10], this is fundamentally the same structure. The drastic difference between the two models is in the microscopic nature of this pattern, with the introduction of a modulation with a wavevector $b^*/3 + \kappa$. Finally the LAS is attributed to the domains of a commensurate orthorhombic $b^*/3$ phase, but without reference to a specific TEM picture. On the inc side, the EQT patches are not mentioned. As further support of their ferroelastic model, Aslanyan *et al* [11] have cited our γ-ray observation of a splitting of the lattice Bragg reflection in the final stage of the coexistence state [48]. Although this is a real effect, this measurement is a single observation on an undefined region of the coexistence state, which could also be due to macroscopic coexistence strains, as previously suggested.

4.2.3. The Saint-Grégoire et al model. Our main criticism on their work [10] is that the existence of a new ELT phase, stable in a 0.1 K range above T_c, is in contradiction with

our previous experiments. Indeed in all TEM pictures, the ELT pattern occurs at a lower temperature than the EQT patches; but, as reported in table 2, the large-period objects, corresponding to EQTs (and eventually to some ELTs), occur only after the nucleation of the α-phase at T_c. It is then clear that the ELT structure exists only in a metastable state, during the coexistence of the two phases. There is a second argument related to the 1 K thermal hysteresis of the α–inc phase transition. If the ELT structure is identified with the SAS region, it must also be present upon heating around $T_h = T_c + 1$ K, where the opalescence is also observed. However, a phase existing in a 0.1 K range cannot be stable at the same time at two temperatures different by 1 K, and it is clear that the ELT structure present at T_h upon heating is in a non-equilibrium state, in the vicinity of the α-phase. Thus one could think that the ELT structure, observed upon cooling above T_c, is also in a metastable state, in the same way as the state existing at T_h. If their model is valid for macroscopic samples, it would be possible to observe the SAS before the appearance of the LAS, and the ELT phase stable in a 0.1 K range would spread over the whole sample, two features which have not been reported at the present time. There is however a possibility of conciliating the results of macroscopic experiments with the claim of Saint-Grégoire et al: in the thin samples used for TEM, the coexistence conditions may be completely modified and the ELT phase may be stable in the finite temperature range, shown in figure 4(c).

Finally on the theoretical side, Saint-Grégoire et al [10] used the domain wall approximation, where parallel walls are separated by a large distance and have only a small exponential interaction. This model is valid only for the well separated walls existing at a continuous lock-in transition, while in quartz the lock-in transition to the α-phase is clearly discontinuous. In his recent work [51], Saint-Grégoire admits the limitation of his model. However, it is possible that these theoretical considerations may be relevant for the larger periods of the non-equilibrium state, given in table 2, and may explain the morphological instabilities between EQT, ELT and IRP patterns.

In the initial work of Saint-Grégoire et al [10], there was an awkward situation for the LAS: although they cited the opalescence of Yakovlev et al [9] (corresponding to LAS), they applied their ELT model explicitly to the SAS, discovered much later [37], and no model of the LAS was proposed. In his recent contribution [51], Saint-Grégoire has developed a specific explanation for the LAS, which is now attributed to the irregular triangular structure of figure 3(c_2), observed by Snoeck and Roucau [47] on the α-phase side of the transition region. This is probably a particular example of the IRP structure that we use in our model. However, Saint-Grégoire considers that the triangles, which must have different values of the order parameter to produce LS, are not Dauphiné twins (which in principle are related by a strict symmetry operation) but some undefined intermediate structure. On the other hand, we propose to consider these non-periodic triangles as non-equilibrium Dauphiné twins with discontinuous increase of the absolute values of the order parameter η. The difference between the two approaches seems rather semantic. The major consequence is a different localization of the α–inc phase boundary in the TEM pictures: we find that this is a smooth line following the small side of the large triangles, while Saint-Grégoire obtains this as a zigzag line following the large external sides of the triangles. However, it is not clear whether there is a well defined interface between the inc phase and the α-phase in the coexistence state, as it is possible to have a continuous passage from a large-period inc structure to Dauphiné twins. There may be some complication when one considers the three-dimensional structure, with possible variations along the Z-axis, as observed in several TEM experiments [21, 44, 46].

4.3. The origin of the refractive index modulation

Finally we discuss the origin of the refractive index variations proposed in the three models to explain the origin of SAS and LAS opalescence phenomena.

In our model of EQT patches, the variation of the refractive indices is mostly due to the discontinuous increase of the order parameter η in the non-equilibrium EQT and IRP regions: η can increase from a small value in the $3q$ inc phase to a large value in the α-phase, producing very convenient variations of the refractive indices. If the EQT patches have the same diameter of 0.1 mm as the rotation domains of the inc $3q$ phase, there are about 20 EQT patches in a SAS region with a thickness of 2 mm. If as estimated by Shustin *et al* [39], the discontinuity of the refractive indices between different scattering centres of the SAS region is 1×10^{-5}, the total variation of the refractive indices is 0.2×10^{-3}, which is 1/5 of the total discontinuity observed at T_c between the α- and the $3q$ inc phases.

As regards the ELT model of Saint-Grégoire *et al* [10], the strong criticism of Aslanyan *et al* [11, 13] of the weakness of the ferroelastic effect in an equilibrium ELT phase may be valid. However, recently Saint-Grégoire *et al* [60] gave a new evaluation of the variation of the refractive indices in their ferroelastic model, using the domain wall approximation. They claim that the effect may be large enough to produce the SAS.

Our evaluation of the model of Aslanyan *et al* [11] is rather unfavourable, as there is absolutely no evidence for the existence of a modulation around $b^*/3$. However, according to their model, this is not a definitive proof, as this modulation cannot be observed in the $3q$ inc phase! But at least one could hope to observe the $b^*/3$ superstructure of the commensurate phase and a precursor diffuse scattering around $b^*/3$ in the β-phase. One of the main justifications for the introduction of a $b^*/3$ modulation was the small value of the change of the refractive indices for the ferroelastic domains of an inc ELT phase, with a small wavevector. However, as we have proposed that the SAS is due to non-equilibrium rotation patches, the argument of the weakness of the ferroelastic effect is now not very relevant. Finally we mention our strong disagreement with two other claims of Aslanyan *et al* on a larger range of the $1q$ inc phase [56] and on the components of the inc modulation [61].

4.4. Overview and perspectives

We think that our model explains qualitatively the main features of the quartz opalescence and that the role of the non-equilibrium EQT patches and Dauphiné twins in explaining respectively SAS and LAS is rather plausible. However, there is some uncertainty as regards the role of the ELT region and the nature and position of the α-phase boundary. The next but difficult step would be to give a quantitative theoretical evaluation based on the effect of stress or of a gradual variation of the order parameter in the coexistence state by using the classical model of the inc phase of quartz [18]. It would also be important to determine the increase of the order parameter from the $3q$ inc phase to the α-phase and in particular to determine whether there is a discontinuity of the physical properties between the inc and the α-phases, in the coexistence state.

Although our model appears rather plausible, the final answer will come from new experimental investigations. Optical studies will be useful to get more accurate knowledge of the opalescence phenomena in relation to the various models. The most important point will be to determine whether a SAS region, extending throughout the whole sample, can be observed before the nucleation of the α-phase. This is a crucial observation for the validity of the two models with stable ferroelastic phases. Due to the variability of previous results in the boundary region, new TEM experiments would also be useful to test the reproducibility of the observed pictures, in particular for the 2D-ELT blocks. A puzzling point is that at

the present time, there is no evidence of the existence of the ELT structure in macroscopic samples. This question can be tested by a diffraction experiment performed with a narrow x-ray beam in a coexistence state. From our previous results [48,57], there is only a very small probability of observing an equilibrium phase in a finite temperature range above T_c. On the other hand, a spatially resolved x-ray diffraction study on a coexistence state, stabilized in a temperature gradient, as realized in previous diffraction experiments [44,48] can be performed. This experiment would differentiate the regions with Dauphiné twins from the regions with an inc phase. In an ELT structure, one can expect to detect satellites, corresponding to the small- and large-ELT sides, as already observed from the diffraction of an electron beam in thin TEM samples [21]. Finally, one can hope to get some evidence for the existence of the $b^*/3$ modulation, predicted by Aslanyan *et al* [11], and of a ferroelastic splitting of the usual lattice peaks.

5. Conclusions

Our knowledge on the α–β transition of quartz was greatly improved by the discovery of the $3q$ inc phase 20 years ago. Although the 1.4 K extension of the inc phase is small, it is the final stage of the anomalous softening of the high-temperature phase and the initial stage for the increase of the order parameter η. The ultimate dramatic step of the transition occurs in an even smaller temperature range of a few mK: after nucleation of the α-phase, there is a coexistence state where the most spectacular anomaly is the existence of an intense opalescence, just before the return to a normal behaviour in the α-phase. The possibility of a disordered structure in the β-phase has been debated for a long time, although recent contributions are in favour of an ordered structure [62,63]. However, the behaviour of the β-phase is rather anomalous: for example the elastic constants [64] and thermal expansion [65] have anomalous variations in a temperature range of $50°$ above the transition, probably due to large fluctuation effects.

In our present model, the introduction of non-equilibrium EQT rotation patches and IRP microtwins is a great improvement which leads naturally to SAS and LAS. For the ferroelastic ELT model introduced by Saint-Grégoire *et al* [10] to explain SAS, there is no evidence of the existence of this region in macroscopic samples and it seems that the magnitude of the ferroelastic effect would be rather small. On the other hand, the LAS model of Saint-Grégoire is now rather similar to our LAS model, as both models attribute the LS to the presence of an interfacial structure, observed in the presence of the α-phase. We further propose that these structures can be identified as non-equilibrium Dauphiné twins. As regards the model of Aslanyan *et al* [11], the introduction of a modulation around $b^*/3$ appears as a rather hypothetical and unnecessary mechanism to explain the quartz opalescence. (Recently, Saint-Grégoire *et al* [66] have performed a new TEM measurement of the quartz transition, showing absolutely no evidence for the presence of a modulation around $b^*/3$.)

We think that the introduction in our model of non-equilibrium structures, EQT rotation patches in the inc phase and IRP Dauphiné microtwins in the α-phase, is a simple way to explain the existence of two LS phenomena in two contiguous regions. It seems that after 45 years of mystery, our non-equilibrium model is now a good starting point for explaining the origin of the quartz opalescence.

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