The Elongated -Triangle (*ELT*) Phase in Quartz as an Incommensurate Ferroelastic

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Abstract: We analyse ferroelastic blocks and deformations in the quartz *ELT* phase in the frame of domain textures model. We show that the estimation of the ferroelastic strain is consistent with the conclusion driven form the small angle light scattering and show that the ferroelastic blocks are the origin of optical inhomogeneities.

keywords: *ELT phase, domains, ferroelastic strains, light scattering, quartz*

I. INTRODUCTION

The *ELT* phase in quartz has been observed unambiguously as a new phase several years ago [1], and we proposed it to be constituted in ferroelastic blocks responsible for the intense anomalous light scattering. Remember that this phenomenon (in fact a "Right-Angle light Scattering", RAS) was discovered at α-β phase transition in 1956 by Yakovlev et al [2], and that there exists also a Small-Angle Scattering (SAS) [3,4] localized in temperature few hundredths of degree above. Studies [5] of the SAS revealed the presence of optical inhomogeneities elongated along the high-symmetry axis of quartz, the characteristics of which allowed to discard Dolino' s model[6] of coexistence between α and β phases. However the cause of the spatial variation of optical indices in the crystal remained unclear since that time.

Around 1980, the *IC* phase in quartz, predicted earlier by Aslanyan and Levanyuk [7], was observed. However this new fact did not allow to understand the origin of optical inhomogeneities because in the largest part of its temperature extension, the *IC* state has a sixfold symmetry (this phase is now designed as *EQT* phase for Equilateral-Triangle phase because it is visualized in electron microscope as a pattern of such triangles associated with the modulation. Besides, the first evidence of the *IC* state was in fact given by TEM [8,9]) that leads to the homogeneity of optical properties, both *EQT* blocks having the same birefringence.

The *ELT* phase, because of its lower symmetry, has blocks with different optical properties related to the ferroelastic distortions that spontaneously occur.

The aim of this paper is to describe the ferroelastic properties of this *ELT* phase, and to give an estimation of the magnitude of the spontaneous deformation.

II. SYMMETRY, DOMAIN TEXTURE, AND BLOCKS

The question of the tensorial properties of *DW*s in quartz has first been treated by Walker and Gooding [10] who showed that there occur displacement fields on both sides of the central part of the wall, and that the *DW*s should carry a polarization along z. These authors showed also that equilibrium *DW*s should not be normal to the y-type axes (lost in α phase) but are deviated by an angle ε of rotation around the z-axis [11]. These properties can also be deduced from more formal techniques based on left coset decompositions of groups [12,13] that show that the symmetry of a single *DW* is 2_z.

The available *DW*s with low (negative) energy are thus those shown in Fig. 1, where *DW*s represented as full and dashed lines are of opposite spontaneous polarizations, as objects related eg by the 2_{yi} symmetry operation.

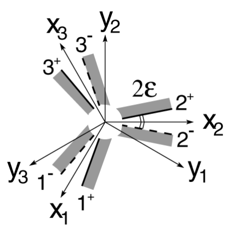
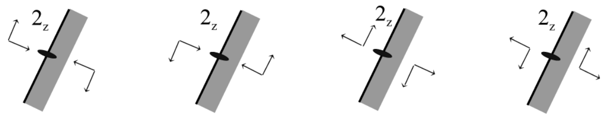


Figure 1: Domain Walls of lower energy. Dashed and full lines refer to *DWs* rotated by opposite angles around z, who carry antiparallel polarization along z. Grey and white colors indicate areas with opposite values of *OP* η.

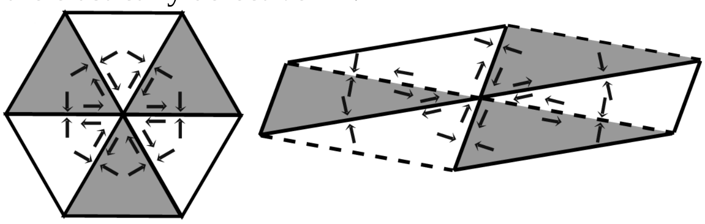
With such a symmetry, the configuration of the displacement fields on both sides of the *DW* may be that shown in Fig. 2a. Of course the symmetry allows to deduce the correspondence of fields on both sides but does not allow to say in which sense the displacements occur, so that several cases as given in Fig. 2a-d are a priori possible but not equivalent. Only one among them can occur. In the following we assume that it is that shown in Fig. 2a.



(2a) (2b) (2c) (2d)

Figure 2: The different configurations of the displacement field (arrows) around the represented wall.
Displacement fields are expressed with respect to an origin taken in the center of the wall. The represented configurations are not physically equivalent and only one occurs. In the following displacement fields are supposed to be according the 2a situation.

Two regular patterns can be built with such *DW*s as shown in Fig. 1: they respectively correspond to the *EQT* phase (Fig. 3a) and to the *ELT* phase (Fig. 3b). Both structures are characterized by elastically non-defective vertices: as expected from the symmetry of these vertices, the Burger vectors for loops around them are zero. All other possible vertices are elastically defective [14].



(3a) (3b)

Figure 3: *EQT* and *ELT* textures and corresponding displacement fields

Now pay attention to elastic properties of these phases. Because displacement fields compensate in the *EQT* structure, the result is a tensile strain and therefore no ferroelasticity occurs.

In the *ELT* phase, the situation is different: the domain texture symmetry is $P2_z$. A monoclinic ferroelastic distortion is therefore permitted. With the symmetry lowering from $6_z2_x2_y$ to 2_z, there occur 6 symmetry-equivalent realizations of the *ELT* phase (Fig. 4), namely 6 textural blocks related by symmetry operations lost in *ELT* phase. These operations are 3_z, 3_z^2, 2_{xi}, and 2_{yi}. The blocks may be distinguished by their ferroelectric and their ferroelastic properties, namely by the sign of P_z and the strain tensor components ($u_{x_ix_i}$ - $u_{y_iy_i}$) and $u_{x_iy_i}$. It is noteworthy that the ferroïc properties of the *ELT* arise from the tensorial properties of the *DW*s: a spontaneous polarization occurs because the lengths of *DW*s represented by dashed and full lines are different, and the ferroelasticity is due to the non-compensation of displacement fields in this low-symmetry texture.

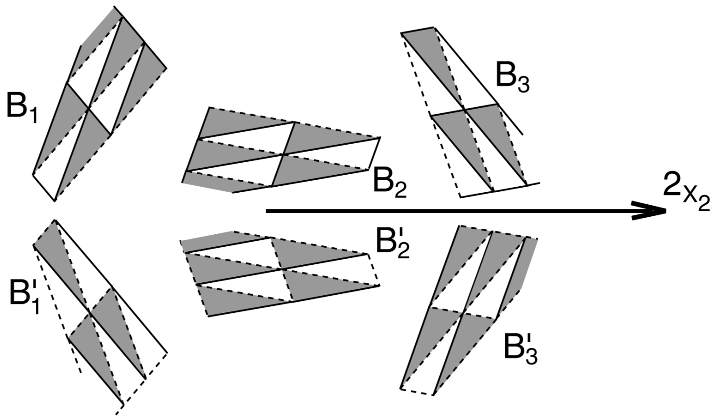


Figure 4: The 6 textural blocks of the *ELT* phase.
The 3 upper blocks are related through 3-fold operations and belong to the same ferroelectric domain. B'$_1$ B'$_2$ B'$_3$ are obtained from the formers by eg: 2_{x2}.

The *ELT* phase is the unique ferroelectric and ferroelastic *IC* phase that is known. It is also a new state in that sense that the associated *k*-star is double, which situates this phase in between usual *IC* phases and quasicrystals.

III. FERROELASTIC PROPERTIES

Recently we confirmed by a *TEM* study [15] that the order parameter (*OP*) η has a soliton-like profile in the *ELT* phase and we therefore use the description in terms of *DW*s as in our preceding work [1]. We show below that this type of distribution $\eta(r)$ where η varies mainly within the domain walls of width $L \sim 5nm$ and stays uniform inside "$+\eta_o$" and "$-\eta_o$" *ELT* domains [15] results in the anisotropy of refraction index (due to ferroelastic deformation) that allows to explain the *SAS*. The deformation is due to the coupling of the *OP* gradient with the strain tensor u_{ij} that occurs through several terms. The largest deformation results from the coupling of u_{ij} with squares of the order parameter gradients η_x, η_y written as [16]:

$$F_{coupl} = r_1\left[\left(\eta_x^2 - \eta_y^2\right)\left(u_{11} - u_{22}\right) + 4\eta_x\eta_y u_{12}\right] \qquad (1)$$

To know the distribution of strain inside the crystal one should solve the problem of the elasticity theory where the stress is given by $\sigma_{ij}^d = \delta F_{coupl} / \delta u_{ij}$. The wavelength of the scattered light: (400-500 nm) is, however, much larger than the characteristic size of domains $D \sim 50nm$ and only the *average* shear deformation is relevant. To estimate it, we assume that the crystal is subjected to an uniform stress $\overline{\sigma}_{ij}$ that is obtained by the uniform redistribution of the domain wall stress σ_{ij}^d into the bulk of the crystal:

$$\overline{\sigma}_{ij} \sim \frac{L}{D}\sigma_{ij}^d \sim \frac{L}{D} r_1 (\nabla\eta)^2 \qquad (2)$$

$\nabla\eta$ may be evaluated as $\nabla\eta \sim 2\eta_0 / L \sim 10^{-2}$, the amplitude of the uniform *OP* inside *ELT* domains being roughly estimated as $|\eta_0| \sim 0.3Å$. The shear deformation is provided by the counterbalance between the internal stress $\overline{\sigma}_{ij}$ and the restoring effect of the elastic energy :

$$F_{el} = \frac{c_{11} - c_{66}}{2}\left(u_{11} + u_{22}\right)^2 + \frac{c_{66}}{2}\left(\left(u_{11} - u_{22}\right)^2 + 4u_{12}^2\right) \qquad (3)$$

Equating $\overline{\sigma}_{ij}$ to the elastic shear stress $\sigma_{ij}^{el} = \delta F_{el} / \delta u_{ij}$, we estimate the average shear distortion :

$$\overline{u}_{11} - \overline{u}_{22}, \overline{u}_{12}^2 \sim \frac{L}{D}\frac{r_1}{c_{66}}(\nabla\eta)^2 \sim 10^{-5} \qquad (4)$$

The anisotropy of the refraction index is estimated using the optical-mechanical coefficient $\chi \sim 0.1^3$ as:

$$\Delta n \sim \chi(\bar{u}_{11} - \bar{u}_{22}, \bar{u}_{12}) \sim 10^{-6} \qquad (5)$$

This value is only 10 times smaller than the birefringence extracted from experiment [6]. We consider this estimation as satisfactory, taking into the account that several constants (as the ratio r_1/c_{66}) were only roughly estimated here and that on another hand Δn was observed to be sample dependent.

IV. CONCLUSION

We performed an analysis and estimation of deformations in the *ELT* phase using the framework in which this phase is modelled as a dense and regular packing of domains and domain walls (*DW*s). The tensorial properties of *DW*s determine the properties of the material and the displacement fields. The stress that occur within the walls results macroscopically in a global ferroelastic deformation. The estimated value of deformation confirm our preceding proposition that ferroelastic *ELT* blocks are at the origin of the optical inhomogeneities responsible for the small angle light scattering. Our approach is different from that of Aslanyan, Shinegari, Abe [17] who assumed a sinusoidal modulation of the order parameter and obtained values of strain and birefringence four orders of magnitude smaller than expected. Their approach, however, may be rejected on the basis of a recent *TEM* results that demonstrate that there occurs a sharp soliton-like profile of the order parameter in the *ELT* phase.

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