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**COMMENT**

# Comment on 'Inhomogeneities and birefringence in quartz'

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**Abstract.** We comment on the role of the novel incommensurate elongated-triangle (ELT) phase in the huge light scattering in quartz at small angles that was observed more than 40 years ago at the $\alpha$–$\beta$ phase transition and was associated with optical inhomogeneities of unknown nature. The relation of these inhomogeneities with the differently oriented ferroelastic blocks of the ELT phase proposed by us and co-workers in a previous publication was misinterpreted and criticized in a recent article by Aslanyan *et al* (Aslanyan T E, Shigenari T and Abe K 1998 *J. Phys.: Condens. Matter* **10** 4577), who claimed also that the lock-in occurs at $q \neq 0$. Responding to their criticism, we claim that the ELT blocks do have ferroelastic properties which induce the inhomogeneities of optical indices and that the lock-in occurs at $q = 0$.

The question of the anomalously strong light scattering at small angles in quartz near the $\alpha$–$\beta$ structural transition has been discussed since its discovery in 1956 [1] in a lot of papers and has led to controversies persisting to recent years [2]. It appeared finally that its origin is the presence of some static inhomogeneities of cross section ~1000 nm elongated along $z$ with dielectric constant variation $\varepsilon_{xx} - \varepsilon_{yy} \sim 5 \times 10^{-5}$, the nature of which was unclear. More recently, an incommensurate (IC) phase was predicted at the $\alpha$–$\beta$ transition by Aslanyan and Levanyuk [4] and then discovered experimentally in a temperature interval of ~1.5 K [8, 19]. The phenomenological approach was thereafter improved by considering several distinct incommensurate phases and the possibility of deviation of modulation vectors from crystallographic directions [3, 10]. Observed by means of transmission electron microscopy (TEM), the IC phase appeared first as a pattern of regular equilateral-triangular (EQT) Dauphiné twins (characterized by opposite values of the order parameter $\eta$) [14]. However, the Dauphiné twins in an EQT phase cannot be associated with the observed inhomogeneities since the optical properties depend on the square of $\eta$ and are therefore identical. On the other hand, the inhomogeneities cannot be due to the orientational variants (two in number) of the EQT phase because the associated optical indicatrix is isotropic around the $z$-axis, due to the sixfold symmetry of this phase [18].

Another IC phase was observed in a small temperature interval of 0.1 K between the EQT and $\beta$-phases [16]: this is a $1q$-phase (stripe phase) but, in spite of its ferroelastic character, it cannot be associated with the strong light scattering, which, according to current knowledge, occurs 1 K below, just above the $\alpha$-phase [1].

Two years ago, we and some colleagues published evidence for the existence of one more IC phase that exists exactly in the region of the strong light scattering, between the lock-in

$\alpha$-phase and the EQT phase, and involves discommensurations forming a pattern of elongated triangles (ELT) [5, 6]. The following sequence of the IC phases at the $\alpha$–$\beta$ transition was proposed:

$$\alpha\text{–ELT–EQT–}1q\text{–}\beta. \tag{1}$$

The analysis of the average symmetry of the ELT phase (point group $2'_z$) shows that it should be ferroelastic and ferroelectric, and that the ferroelastic domain walls should be oriented along the $z$-axis. Due to this symmetry, the ferroelastic (macro)domains (that we also called blocks) are characterized by optical indicatrices having an elliptical section in the basal plane (due to the $2'_z$ symmetry). The axes of the ellipse point in different directions in the different ferroelastic domains which are therefore able to produce the spatial inhomogeneities of the refractive index, and we proposed that the blocks of the ELT phase lie at the origin of the huge light scattering in quartz.

In an earlier issue of *Journal of Physics: Condensed Matter*, Aslanyan, Shigenari and Abe published a paper entitled 'On the origin of the inhomogeneities and birefringence in the incommensurate phase of quartz' [7] where they restated our idea that ferroelastic properties of the IC phase in quartz may lie at the origin of light scattering. This led us to write the present comment for the following reasons:

(a) An incorrect view of our publication was given, in particular concerning ferroelastic properties of the ELT phase.
(b) Aslanyan *et al* claimed that they evidenced the ferroelasticity of the IC phase of quartz, not mentioning what the relations with the ELT phase are that we discovered. It appears finally that the phase that they consider coincides with our ELT phase.
(c) The birefringence of the ferroelastic ELT phase, and hence its role in the light scattering, was underestimated due to the inconsistency of the harmonic-wave approximation in the lock-in transition region where this phase appears. This led the authors to propose a lock-in point which has no experimental basis.

Consider first the ferroelasticity of the IC phases in quartz. The first work in this direction, unfortunately not mentioned in the paper by Aslanyan *et al* [7], was done by Walker and Gooding [9], who analysed the EQT phase in quartz in terms of a regular network of domain walls—the discommensurations between Dauphiné twins. Domain walls (figure 1(a)) are parallel to the hexagonal axis $\boldsymbol{z}$ and have six symmetrically equivalent orientations in the basal plane $\boldsymbol{x}$–$\boldsymbol{y}$ [17].

We showed [5] that two regular $3q$-periodic textures of domain walls corresponding either to the EQT or to the ELT phase are possible. The pattern of the EQT phase can have two equivalent crystallographic orientations (figure 1(b)) whereas the pattern of the ELT phase (figure 1(c)) has six orientational variants (and not three as was indicated by Aslanyan *et al*). This leads to the appearance of macrodomains of the long-period IC structures of two different types in the EQT phase and of six different types in the ELT phase that we called (textural) block states in order to avoid any confusion with triangular domains (i.e. Dauphiné twins) of $\alpha$-phase. In equilibrium conditions the size of the blocks (100–1000 nm) is substantially larger than the size of the constituting triangular Dauphiné twins (10–100 nm).

As was first pointed by Walker and Gooding [9], domain walls carry both a polarization along the $z$-axis, and a spatial variation of the displacement field in the plane $\boldsymbol{x}$–$\boldsymbol{y}$. These two effects may result in the ferroelectric and ferroelastic properties of the IC phase. The EQT phase, which is built with walls polarized in the same direction, exhibits a global ferroelectricity that was confirmed by TEM experiments under electric field [15]. The ferroelasticity, however, does not appear there since walls form equilateral triangles and a compensation of distortions occurs whereas, in contrast, the stripe $1q$-phase should be ferroelastic but not ferroelectric.

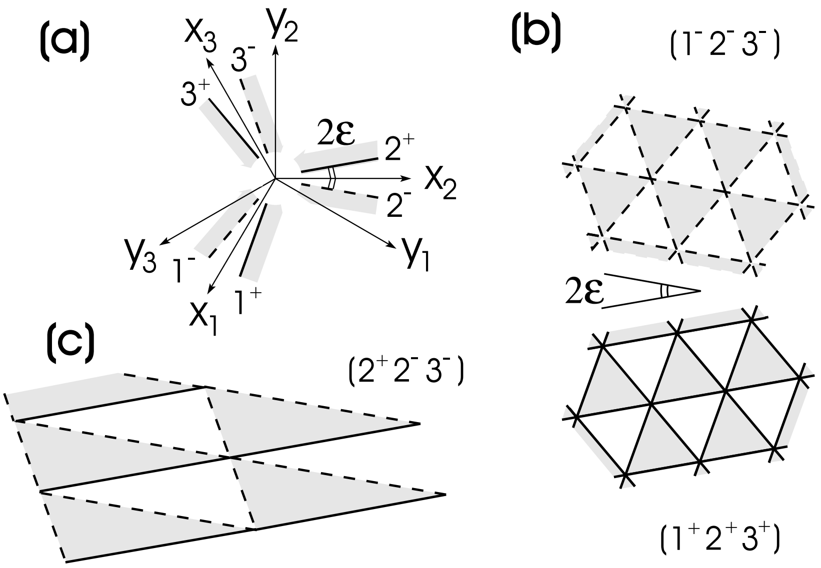

**Figure 1.** Domain walls and domain textures in IC quartz: (a) equilibrium orientations of isolated domain walls, (b) the two block states (orientational variants) of the EQT phase, (c) one of the six block states of the ELT phase. White and grey regions are characterized by opposite values of the order parameter $\eta$; full and dashed lines refer to domain walls rotated away in opposite directions around $z$. The distortions within the walls compensate in the texture of blocks of the EQT phase but not in a block of the ELT phase, which can thus be identified with a ferroelastic (and ferroelectric) domain.

We showed that both a ferroelectric polarization and a global ferroelastic deformation occur in the ELT phase, and '*the ELT ferroelastic blocks have optical indicatrices of different orientation which results in the spatial inhomogeneity of the refraction index*' (from reference [5]).

Although we indicated clearly that the spontaneous deformation is a global property of the regular ELT blocks of typical size 1000 nm that we analysed and observed by means of transmission electron microscopy over a large region of the crystal under the special condition of a small thermal gradient (figure 1 of [5]), Aslanyan *et al* wrongly interpreted it as ferroelasticity of separate elongated triangles: '*The spatial average of such strains over the IC period is, in general, zero and therefore the effect discussed by Saint-Grégoire et al cannot be considered as ferroelasticity. In other words, each triangle in the figure was identified as a ferroelastic domain, while each such triangle is only a part of the IC period*' [7].

A confusion was therefore made by these authors between blocks and domains. Moreover the TEM image analysed by Aslanyan *et al* (their figure 2(a)) is obtained under the condition of such a huge thermal gradient (estimated from their TEM figure to be around 10 K $\mu$m$^{-1}$) that a chaotic domain wall texture appears at the $\alpha$−EQT interface instead of the regular ELT phase which is only observed in very careful experiments [5]. In other words the bottom of this figure can be considered as an ELT phase where the size of the blocks is of the same order as the size of the ELT Dauphiné twins. This non-equilibrium state was called 'irregular triple-*k* structure' or 'irregular triangles', but the same statement about ferroelasticity as that we made previously regarding the blocks of the ELT phase was given: '*Ferroelasticity appears only in the case in which the IC lattice cell acquires non-zero strains as a whole, . . . this possibility is introduced in the present paper*' [7].

To estimate the birefringence from the blocks of the ferroelastic incommensurate phase, the lock-in order parameter $\eta$ was approximated by Aslanyan *et al* by a superposition of three harmonic waves:

$$\eta = \eta_0 \sum_{1,2,3} \cos(\boldsymbol{k}_i \cdot \boldsymbol{r} + \phi_i) \tag{2}$$

which results in a phase which coincides topologically with our ELT phase but describes it in the different framework of the harmonic-wave approximation. Then, considering the coupling of the gradients of the modulated order parameter (2) with crystal strain $u_{ij}$:

$$r_1(\eta_x^2 - \eta_y^2)(u_{11} - u_{22}) + 4\eta_x\eta_y u_{12} \tag{3}$$

they deduced the spontaneous distortion

$$(u_{11} - u_{22}), u_{12} \sim \frac{r_1}{c_{66}}(k\eta_0)^2 \sim 10^{-8}. \tag{4}$$

Assuming that $r_1/c_{66} \sim 1$ and that $\eta_0 \sim 10^{-2}b$, $k \sim 10^{-2}k_b$ ($b, k_b$ are the real and reciprocal-lattice parameters) these authors estimated the distortion: $(u_{11} - u_{22}), u_{12} \sim 10^{-8}$. The corresponding variation of the birefringence $\sim 10^{-8}$–$10^{-9}$ obtained from the optical–mechanical coefficient for quartz, $\sim 0.1$, is four orders of magnitude smaller than the value necessary for explaining the optical inhomogeneities ($5 \times 10^{-5}$).

Note, however, that this value was substantially underestimated by Aslanyan *et al* because the harmonic-wave approximation, usually used for the incommensurate phase of type II, is inappropriate in the region of the ELT phase. According to TEM observations, the order parameter $\eta$ in this region clearly acquires a soliton-like profile [11] and higher-order satellites were observed [13], whereas the admixture of higher harmonics in an IC phase of type II should not exceed 3% [12] close to the lock-in transition. The domain wall approach, that allows one to explain the existence of the ELT phase [5], is more appropriate for this region. The gradients of the order parameter $\eta_x$ and $\eta_y$ inside the domain wall are significantly larger than those used in (3) in the harmonic-wave approximation, which enhances the resulting ferroelastic deformation of the ELT structure. On the basis of results obtained by TEM, the total deformation averaged over the crystal volume is found to be [11]

$$(u_{11} - u_{22}), u_{12} \sim 10^{-5}. \tag{5}$$

This estimate is substantially larger than that from (4) and is in agreement with the experimental expectation.

The too-small estimate of the birefringence variation obtained by Aslanyan *et al* for the ELT phase led them to propose another value for the modulation wavenumber $k$. Considering the result following from (4) that the distortion of the modulated phase varies as $k^2$, they concluded that the lock-in should occur at $k_c = \frac{1}{3}k_b$ rather than at $k_c = 0$. According to their calculations of Debye–Waller factors, they made the interesting suggestion that fundamental and second harmonics are not observable, and that the observed satellites are the third-order harmonics of $\frac{1}{3}k_b$.

However, as we have shown, the realistic estimate based on the domain texture does give a value of the birefringence variation in the ELT phase which is compatible with experiment, and therefore the suggestion of another value of $k$ is not necessary. Moreover there is no experimental evidence at all of any lock-in at $\frac{1}{3}k_b$. In particular, the assignment of some region of the sample to a lock-in at $\frac{1}{3}k_b$ has no basis. No superlattice reflection at such commensurate positions was observed by any means—neutron, x-ray, or electron diffraction—in the region of the $\alpha$–$\beta$ transition.

To conclude, three IC phases are known in quartz: the stripe phase (ferroelastic and not ferroelectric), the EQT phase (ferroelectric and non-ferroelastic) and the ELT phase (both ferroelastic and ferroelectric) and the lock-in does occur at $k = 0$. The ELT phase—with its ferroelastic structural blocks—is the only candidate suitable for producing the optical inhomogeneities that cause the huge light scattering in quartz observed more than 40 years ago:

(i) it appears in exactly the same temperature region, i.e. 0.1 K above the lock-in temperature;
(ii) ferroelastic blocks have a size ~1000 nm and a shape consistent with that of optical inhomogeneities;
(iii) the estimate obtained from the analysis of the properties of the ELT blocks is in good agreement with light scattering data.

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