Comment on the "Origin of the opalescence at the $\alpha \leftrightarrow \beta$ transition of quartz: role of the incommensurate phase studied by synchrotron radiation"

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The present paper is a comment on the interpretation by Dolino et al. of their recent observations in quartz. In the paper, from the diffraction experiment using synchrotron radiation, the authors showed that the incommensurate (IC) modulation wavevector in quartz becomes extremely small in the region of the sample close to the boundary between the IC phase and the $\alpha$-phase. In this region, where the two phases coexist in the same sample, very intense light scattering is observed. Therefore, it is very important to consider how the intense light scattering is related to the reported extraordinary long period modulation.

In the following, we show that (i) the observed long-period IC modulation in quartz is a pure transversal acoustic (TA) modulation, including neither longitudinal acoustic (LA) component nor the optic mode component. (ii) A long-period acoustic modulation cannot appear spontaneously as a result of the IC phase transition associated with the acoustic mode softening, and the mechanism of its formation should be understood. (iii) Such a modulation cannot be at the origin of any observed light scattering anomalies contrary to the interpretation by Dolino et al.

The consideration below is mainly based on the observations by Dolino et al. of the IC satellite reflections in the elastic neutron diffraction, and their expected evolution in view of the recent observations in the synchrotron radiation. As observed (see Fig. 1), near the Bragg reflections (100), (200) ... the satellites, corresponding to the IC vector $k$ parallel to the main Bragg reflection vector (100), are systematically absent, i.e. four satellites are observed instead of six. Similar observations by Gouhara and Kato demonstrated that the IC modulation in quartz is mainly of an acoustic character, with a small (of about 0.1 fraction) optical atomic displacements component. The analysis carried out by the present authors, based on the comparison of the IC satellites near the (100) and (10m)-type Bragg reflections, showed that the IC modulation in quartz is a pure TA modulation, including, as one of its components, the transversal $u_y$-displacements. The contribution of the TA $u_y$-displacements to the diffraction was interpreted by Gouhara and Kato as that from a small optical component. The existence of $u_y$-displacements was also demonstrated by the recent MD calculations. Below we bring new arguments, unambiguously demonstrating the TA character of the IC modulation in quartz. However, contribution of a long-period acoustic modulation to the dielectric constant’s components (i.e. to the light scattering) is proportional to the square of the IC wavevector, and therefore it must be negligibly small for the small IC modulation vectors observed in quartz ($k < 0.03a^*$ and decreases on cooling, according to the recent observations, down to 0.002$a^*$).

We show that in the case if the IC modulation contains an optic mode displacements component, an intense IC satellite reflections should necessarily appear in the positions of the missing satellites (in particular, near (300) in Fig. 1).

Let us assume that the IC modulation in quartz, however, contains an optical component. In such a case, the long-period triple-$k$ IC modulation of the quartz’s $\alpha \leftrightarrow \beta$ transition parameter $\eta$ necessarily should induce a longitudinal acoustic (LA) modulation with a large amplitude $u_{0\eta}$. The amplitude $u_{0\eta}$ of such LA modulation should be of the same order of magnitude as that for the $\eta$-modulation for the IC vectors $k \approx 0.03a^*$, and for the IC vectors $k \approx 0.002a^*$ (near the transition to the $\alpha$-phase) it should increase up to $\sim 10$ times (the corresponding diffraction satellites should grow in intensity up to $\sim 10^2$ times). As a result, six intense IC satellites should be induced by the LA modulation instead of the four satellites near any (100) reflection.

The elastic strain dependent part of the quartz’s thermodynamic potential is of the form:

$$
\int \left\{ a \left[ \frac{\partial u_{xx}}{\partial x} - \frac{\partial u_{yy}}{\partial y} \right] + \frac{c_{11} - c_{66}}{2} (u_{xx} + u_{yy})^2 + \frac{c_{66}}{2} \left( (u_{xx} - u_{yy})^2 + 4u_{xy}^2 \right) \right\} dV
$$

where $u_{xy}$, $u_{xx}$, $u_{yy}$ are the elastic strains, $a$ and $r$ are
some coefficients of expansion, which are of an atomic order of magnitude. For the triple-\( k \) IC optical modulation
\[
\eta(R) = \eta_0 \cos(\mathbf{k} \mathbf{R} + \varphi) + \eta_0 \cos(\mathbf{k}_1 \mathbf{R} + \varphi_1) + \eta_0 \cos(\mathbf{k}_2 \mathbf{R} + \varphi_2)
\]
with \( \mathbf{k} + \mathbf{k}_1 + \mathbf{k}_2 = 0 \), and for the acoustic displacements vector \( \mathbf{u} = \mathbf{u}_l + \mathbf{u}_t \), presented as the sum of the longitudinal \( \mathbf{u}_l \) (along the IC vector \( \mathbf{k} \)) and transversal \( \mathbf{u}_t \) displacements, one can minimize Eq. (1) with respect to \( \mathbf{u}_1 \), and obtain an equilibrium LA modulation wave:
\[
\mathbf{u}_l = u_{l0} \sin(\mathbf{k} \mathbf{R} + \varphi_1 + \varphi_2) + u_{l0}' \cos(\mathbf{k} \mathbf{R} + \varphi),
\]
with the amplitudes
\[
u_{l0} = \frac{2\pi\eta_0^2}{c_{11} k} \quad \text{and} \quad u_{l0}' = \frac{\alpha \eta_0 \cos 3\phi}{c_{11}},
\]
where \( \phi \) is the angle between the \( x \) axis and the IC vector \( \mathbf{k} \). In the observed IC structure the angle \( \phi \) is close to \( \pi/6 \), and therefore the corresponding amplitude \( u_{l0}' \) is close to zero and generally neglected. An identical LA IC amplitudes must exist for all the six wavevectors \( \pm \mathbf{k}, \pm \mathbf{k}_1 \) and \( \pm \mathbf{k}_2 \).

Taking into account that the IC wavevector in quartz is very small, and it decreases on cooling from 0.03a* (as in Fig. 1) down to 0.002a* (according to the recent publication by Dolino et al.), one can see the enormous increase of LA modulation’s amplitude \( u_{l0} \) (see the \( k \) vector in the denominator).

The physical reason of the large LA amplitude is very plain. Formation of a long-period acoustic modulation requires a very small energy (this energy is proportional to \( k^2 \), and is tending to zero with \( k \rightarrow 0 \)). Though the acoustic-optic coupling term \( \eta^2 u_{lt} \) in Eq. (1) is rather small, however it is sufficient for inducing an enormous LA amplitude for the small \( k \)-s.

For calculation of the X-ray diffraction scattering amplitude, induced by the IC wave, one should expand the crystals density function as:
\[
F_G \exp[i\mathbf{G} \cdot (\mathbf{R} + \mathbf{u})] \approx F_G \exp[i\mathbf{G} \cdot \mathbf{R}] + iF_G(\mathbf{G} \mathbf{u}_0) \exp[i(\mathbf{G} \pm \mathbf{k}) \mathbf{R}],
\]
where \( F_G \) is the structure factor, corresponding to the Bragg reflection, \( \mathbf{u}_0 \) is the amplitude of the IC acoustic modulation \( \mathbf{u}(\mathbf{R}) \), and the scalar product \( \langle \mathbf{G} \mathbf{u}_0 \rangle = u_{l0} \mathbf{G} \) for the case, when vector \( \mathbf{G} \) is parallel to the IC vector \( \mathbf{k} \) (as for the case of the missing satellites in Fig. 1). The first term in Eq. (2) gives diffraction to the main Bragg reflection \( \mathbf{G} \) with intensity \( \sim |F_G|^2 \). The second term gives the acoustic modulation’s contribution to the satellite reflections \( \mathbf{G} \pm \mathbf{k} \) with intensity \( \sim |F_G(\mathbf{G} \mathbf{u}_0)|^2 \). For the case of \( \mathbf{G} \parallel \mathbf{k} \), this intensity takes the form \( |F_G(\mathbf{G} \mathbf{u}_0)|^2 \), and it extremely increases with \( k \rightarrow 0 \), since, as shown above, \( u_{l0} \) increases as \( 1/k \).

For the case \( k = 0.03a^* \), it is easy to estimate that the satellite intensity induced by \( u_{l0} \) and contributing to the position of the missing satellites in Fig. 1 should be of the same order of magnitude as any intensity, induced by the optical \( \eta \)-atomic displacements. Note that the satellite intensity contributed from the optical component is \( \sim |F_G|\mathbf{G} \mathbf{u}_0| \). In the vicinity of \( 1K \) of the phase tran-
tion, the optical amplitude \( \eta_0 \sim 10^{-2} \eta_{lat} \), where \( \eta_{lat} \) is of an atomic order of magnitude, \( k \sim 10^{-2} a^* \), and subsequently, \( u_0 \) and \( \eta_0 \) are of the same order of magnitude. For the smaller IC vectors \( k \approx 0.002a^* \), \( u_0 \) is larger than \( \eta_0 \) about \( \sim 10 \) times, and the ratio of the corresponding intensities should make \( \sim 10^2 \). In other words, for \( k \lesssim 0.03a^* \) six reflections of about the same intensity in Fig. 1 should be observed. And besides, since the scalar product \( \textbf{G} u_0 \) in Eq. (2) is maximal for the case when \( \textbf{G} \) and \( k \) are parallel, the intensity of the \( \textbf{G} \pm k \) satellites should be larger, than the intensity of the \( \textbf{G} \pm k_1 \) and \( \textbf{G} \pm k_2 \) satellites. In other words, the missing satellites in Fig. 1 should be detected as the most intensive, compared with four other satellites near \( \langle 100 \rangle \).

The only explanation of the systematic observation of four satellites near the \( \langle 100 \rangle \) type Bragg reflections is the TA character of the IC modulation, without optical and LA components, since otherwise, any optical component in the triple-\( k \) modulation necessarily induces a strong LA component, which will contribute to the positions of the missing satellites.

The TA IC structure, which, in fact, exists in quartz, cannot noticeably contribute to the light scattering anomalies, since its effect on the dielectric constant \( \varepsilon_{ij} \) is proportional to \( u_{xy}^2 \) (i.e. to a very small parameter \( k^2 \)), while the light scattering anomalies are observed just when \( k \rightarrow 0 \). So, we do not agree with the interpretation of the light scattering anomalies in quartz by Dolino et al., attributed to the observed IC modulation.

Neither the domains of the IC structure (the adjacent domains with different values of \( k \) in the small-angle scattering zone \( \Delta \)), nor the Dauphine twins observed in the "fog zone" can be responsible for the light scattering in quartz. The latter was discussed in detail and estimated by the present authors earlier, where the origin of the intense light scattering was attributed to the ferroelastic domains. The arguments given above completely contradict the observations and reject the traditional model for the IC transition adopted by Dolino et al.\(^7\).

Finally we introduce another argument, supporting the above discussion. As it follows from the symmetry, in case of the triple-\( k \) IC optical modulation, the dielectric constant’s components \( \Delta\varepsilon_{xx}, \Delta\varepsilon_{yy}, \Delta\varepsilon_{zz} \) are proportional to \( \sim \eta_0^2 \sin(kR + \varphi_1 + \varphi_2) \). Since the magnitude of the IC vector \( k \) decreases down to \( 0.002a^* \), then the light of 500nm or smaller wavelength (i.e. with wavevector \( \geq 0.001a^* \), should diffract in back-direction (or close to it) in such IC modulation. Such a feature, which can be visually detected, is not observed in quartz. This fact also proves, that the LA modulation (and subsequently an optical modulation), which directly follows from the traditional model used by Dolino et al., does not exist in the IC phase of quartz.

It should be mentioned that a long-period acoustic modulation cannot appear spontaneously, as a result of the IC phase transition, associated with the acoustic mode softening. Such a mode softening would have a lot of consequences, including a significant drop in the elastic constant \( c_{66} \), which have never been observed in quartz.\(^8\) One may assume that some latent (driving) phase transition takes place in quartz near the \( \alpha \leftrightarrow \beta \) transition, and the observed acoustic modulation is only a manifestation of this hidden transition. However, a pure TA character of the IC modulation in quartz was sufficiently simply and reliably demonstrated also in the earlier consideration,\(^9\) based on the different arguments. So, it cannot be ignored, and understanding of its origin is of a priority importance in the quartz’s phase transition problem.

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