Character of the incommensurate modulation and the problem of light scattering in quartz near the $\alpha\leftrightarrow\beta$ transition

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(Received 19 July 2005; revised manuscript received 8 February 2006; published 4 April 2006)

It is shown that the observed incommensurate structure near the $\alpha\leftrightarrow\beta$ transition in quartz is a pure transverse acoustic modulation without any optic mode displacements component. Such a long-period acoustic modulation cannot be responsible for the observed light scattering in quartz, contrary to the interpretation by Dolino *et al.* [Phys. Rev. Lett. **94**, 155701 (2005)].

DOI: 10.1103/PhysRevB.73.153101 PACS number(s): 64.70.Rh, 64.60.−i

In the present paper the character of the incommensurate (IC) modulation near the $\alpha\leftrightarrow\beta$ transition in quartz, and its effect on the light scattering anomalies are discussed. Based on the synchrotron radiation and neutron diffraction observations by Dolino *et al.*,[1,2] in the following we show that (i) The observed long-period IC modulation in quartz is a pure transversal acoustic (TA) modulation, without longitudinal acoustic (LA) and optic mode components. (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.*[1]

IC satellite reflections, in general, are contributed by the atomic displacements with respect to the crystal lattice cell (optical displacements), and by the acoustic displacements, i.e., by the displacements of a lattice cell as a whole. (Such a presentation should be viewed only as a simplified geometrical illustration, since the acoustic-optic mode coupling induces distortions of the lattice cells.) In the case of the IC structure of quartz, as shown in the present paper, one can distinguish these two contributions for some satellites, and define some important features of the IC structure. The consideration below is mainly based on the observations of the IC satellite reflections in the elastic neutron diffraction by Dolino *et al.*,[2] and their evolving in the synchrotron radiation diffraction.[1] As observed[2] (see Fig. 1), near the Bragg reflections of the (100), (200),…, type, the satellites, corresponding to the IC vector **k**, which is parallel to the main Bragg reflection vector (l00), are systematically absent, i.e., four satellites are observed instead of six. Similar observations by Gouhara and Kato[4,5] brought them to the conclusion 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,[6] based on the comparison of the IC satellites near the (l00) and (l0 m)-type Bragg reflections, showed that the IC modulation in quartz is a pure TA modulation, including, as one of its components, the acoustic transversal u_z displacements. The contribution of the TA u_z displacements to the diffraction was interpreted by Gouhara and Kato[4,5] as that from a small optical component. However, a pure acoustic IC structure has never been observed in other crystals, and some additional supporting arguments are needed to confirm its existence. Below we bring arguments that unambiguously demonstrate the TA character of the IC modulation in quartz.

Now we show that in the case if the IC modulation contains an optic mode's displacement 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, we show that the long-period triple-k IC modulation of the quartz's $\alpha\leftrightarrow\beta$ transition parameter η necessarily should induce a longitudinal acoustic (LA) modulation with a large amplitude u_{l0}. The amplitude u_{l0} of such LA modulation (which strongly depends on the vector k length) should be of the same order of magnitude as that for the optical η-modulation for the IC vectors $\mathbf{k}\approx 0.03a^*$, and it should increase up to ~ 10 times for the IC vectors $\mathbf{k}\approx 0.002a^*$ (i.e., near the transition to the α-phase 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 (l00) reflection.

The elastic strain dependent part of the quartz's thermodynamic potential is of the form[3]

$$\int\left\{a\left[(u_{xx}-u_{yy})\frac{\partial\eta}{\partial x}-2u_{xy}\frac{\partial\eta}{\partial y}\right]+r\eta^2(u_{xx}+u_{yy})+\frac{c_{11}-c_{66}}{2}(u_{xx}+u_{yy})^2+\frac{c_{66}}{2}[(u_{xx}-u_{yy})^2+4u_{xy}^2]\right\}dV, \qquad (1)$$

where u_{xy}, u_{xx}, u_{yy} are the elastic strains, and a and r are some coefficients of expansion, which are of an atomic order of magnitude. We should minimize this potential with respect to the acoustic displacements u for the case of the triple-k IC optical modulation. Transferring to the Fourier components according to

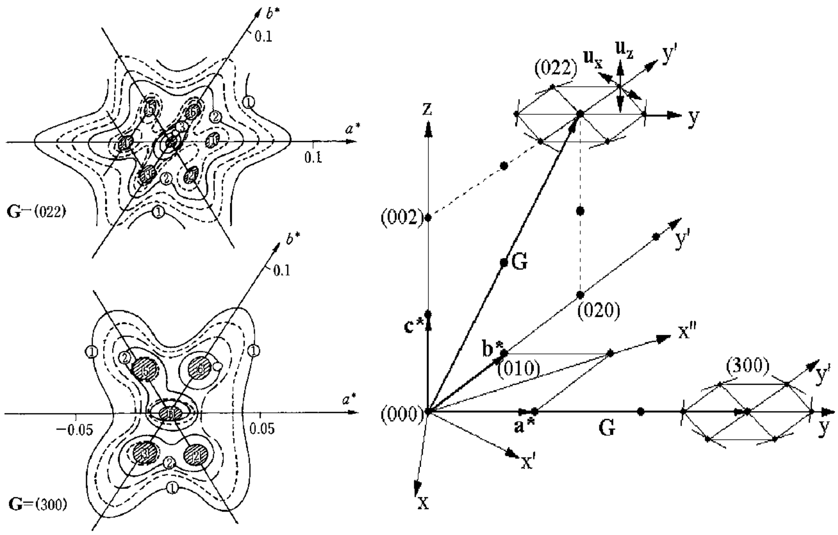

FIG. 1. IC satellite reflections observed near the main Bragg reflections $\mathbf{G}=(022)$ and (300) by Dolino *et al.* (Ref. 2). The two missing satellites along the vector $\mathbf{G}=(300)$, which is parallel to the IC vector $\mathbf{k}$ (i.e., along the a^* axis), provide evidence that the acoustic displacements in the IC wave are perpendicular to the $\mathbf{G}$ vector, and the optic displacements along with the LA displacements are zero in the IC structure. As shown in the present paper, the missing satellites should be observed as the most intensive among the six satellites near the transition to the α phase, if the interpretation by Dolino *et al.* (Ref. 1) is acceptable. The satellites along the a^* axis near (022)-reflection are the contribution from the z component of IC displacements wave of the TA type, since the contribution of the optical displacements to these positions is zero (Ref. 6). On the right side, the acoustic displacements with respect to the crystal's coordinate axes are depicted.

$$\eta(R)=\sum_{\mathbf{k}}\eta_k\exp[i\mathbf{kR}]\quad\text{and}\quad\mathbf{u}(R)=\sum_{\mathbf{k}}\mathbf{u}_k\exp[i\mathbf{kR}],$$

and presenting the acoustic displacements amplitudes $\mathbf{u_k}$ as the sum of the longitudinal $\mathbf{u_{lk}}$ (along the vector $\mathbf{k}$), and transversal $\mathbf{u_{tk}}$ displacements amplitude $\mathbf{u_k}=\mathbf{u_{lk}}+\mathbf{u_{tk}}$, and taking into account that

$$u_{xk}=u_{lk}\cos\phi_k-u_{tk}\sin\phi_k,\quad u_{yk}=u_{lk}\sin\phi_k+u_{tk}\cos\phi_k,$$

where u_{xk} and u_{yk} are the x,y components of the vector $\mathbf{u_k}$, and ϕ_k is the angle between the vector k and x axis, one obtains for potential (1) the form

$$\sum_k ak^2(u_{lk}\cos 3\phi_k-u_{tk}\sin 3\phi_k)\,\eta_{-k}+\frac{c_{11}}{2}k^2|u_{lk}|^2+\frac{c_{66}}{2}k^2|u_{tk}|^2+ir\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''}ku_{lk}\eta_{k'}\eta_{k''}\delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}''). \quad (2)$$

For the case of the observed triple-k IC modulation,

$$\eta(R)=\eta_0\cos(\mathbf{kR}+\varphi)+\eta_0\cos(\mathbf{k}_1\mathbf{R}+\varphi_1)+\eta_0\cos(\mathbf{k}_2\mathbf{R}+\varphi_2),$$

the summations in Eq. (2) run over the three IC vectors k, k_1 and k_2, for which $\mathbf{k}+\mathbf{k}_1+\mathbf{k}_2=0$; the angles ϕ_k, as observed in the experiment, are close to $\pi/6$, $\pi/6\pm2\pi/3$, and hence, $\cos 3\phi_k\approx0$ in Eq. (2), and can be omitted. Taking into account that $\eta_0/2=|\eta_k|=|\eta_{k_1}|=|\eta_{k_2}|$, presenting the complex amplitudes as $\eta_k=|\eta_k|\exp[i\varphi],\ldots$, etc., $u_{\mathbf{lk}}=|u_{lk}|\exp[i\psi],\ldots$, etc., one can minimize potential (2) over the phases ψ,ψ_1,ψ_2 and longitudinal amplitudes $|u_{lk}|$ as follows. The phase multipliers in the last term of Eq. (2), in particular, reduce to the form $\sin(\varphi_1+\varphi_2+\psi)$, which minimizes the equation only when this sine equals to ±1 (depending on the sign of the r-coefficient), i.e., $\psi=-\varphi_1-\varphi_2\pm\pi/2$. Subsequent minimization of Eq. (2) with respect to $|u_{lk}|$ gives

$$2|u_{lk}|=u_{l0}=\frac{2r\eta_0^2}{c_{11}k}.$$

So, we showed that the triple-k optical IC modulation necessarily induces longitudinal acoustic displacements wave

$$\mathbf{u}_l=\mathbf{u}_{l0}\sin(\mathbf{kR}-\varphi_1-\varphi_2).$$

Identical LA IC waves must exist for all the three wave vectors $\mathbf{k}$, $\mathbf{k}_1$, and $\mathbf{k}_2$.

Taking into account that the IC wave vector 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.*[1]), one can see an enormous increase of the LA modulation's amplitude u_{l0} (see the k vector in the denominator).

The physical reason for 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, as energy of any acoustic wave, and is tending to zero with $k\to0$). Though the acoustic-optic coupling term η^2u_{ii} 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 intensity, induced by the IC wave, one should expand the crystals density function as

$$F_G\exp[i\mathbf{G}(\mathbf{R}+\mathbf{u})]\approx F_G\exp[i\mathbf{GR}]+iF_G(\mathbf{Gu}_0)\exp[i(\mathbf{G}\pm\mathbf{k})\mathbf{R}], \quad (3)$$

where F_G is the structure factor, corresponding to the

G-Bragg reflection, $\mathbf{u}_0$ is the amplitude of the IC acoustic modulation $\mathbf{u}(\mathbf{R})$, and the scalar product $(\mathbf{G}\mathbf{u}_0)=u_{l0}G$ for the case, when vector **G** is parallel to the IC vector **k** (as for the case of the missing satellites in Fig. 1). The first term in Eq. (3) gives diffraction to the main Bragg reflection **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 $\mathbf{G}\|\mathbf{k}$, this intensity takes the form $|F_G G u_{l0}|^2$, and it extremely increases with $k\to 0$, 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 η-atomic displacements. Note that the satellite intensity contributed from the optical component is $\sim|F_G G\eta_0|^2$. In the vicinity of 1 K of the phase transition, the optical amplitude $\eta_0\sim 10^{-2}\eta_{at}$, where η_{at} is of an atomic order of magnitude, $k\sim 10^{-2}a^*$, and subsequently, u_{l0} and η_0 are of the same order of magnitude. For the smaller IC vectors $k\approx 0.002a^*$, u_{l0} is larger than η_0 about ~ 10 times, and the ratio of the corresponding intensities should make $\sim 10^2$. In other words, for $k\leqslant 0.03a^*$ six reflections of about the same intensity in Fig. 1 should be observed. And besides, since the scalar product $(\mathbf{G}\mathbf{u}_0)$ in Eq. (3) is maximal for the case when **G** and **k** are parallel, the intensity of the $\mathbf{G}\pm\mathbf{k}$ satellites should be larger, than the intensity of the $\mathbf{G}\pm\mathbf{k}_1$ and $\mathbf{G}\pm\mathbf{k}_2$ satellites. In other words, the missing satellites in Fig. 1 should be detected as the most intensive, compared with four other satellites near (l00).

The only explanation for the systematic observation of four satellites near the (l00) 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.

Concerning the light scattering in quartz, it should be noted that 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's components ε_{ij} is proportional to u_{xy}^2 (i.e., to the parameter k^2, where k is extremely small), while the light scattering anomalies are observed just when $k\to 0$. So, we do not agree with the interpretation of the light scattering anomalies in quartz by Dolino *et al.*,[1] 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)[1] nor the Dauphine twins observed in the "fog zone" can be responsible for the light scattering in quartz. Various mechanisms of light scattering in quartz were discussed in detail and estimated by the present authors earlier,[7] where the origin of the intense light scattering was attributed to the ferroelastic domains. The arguments given above reject the traditional model for the IC transition adopted by Dolino *et al.*[1]

Finally we introduce another argument, supporting the above discussion. As follows from the symmetry, the dielectric constant's components $\Delta\varepsilon_{xx}$, $\Delta\varepsilon_{yy}$, and $\Delta\varepsilon_{zz}$ are proportional to η^2, i.e., for the triple-k optical IC modulation they are proportional to $\sim\eta_0^2\cos(\mathbf{k}\mathbf{R}-\varphi_1-\varphi_2)$. The latter means that for sufficiently small vectors k the crystal can be viewed as an optical diffraction grate. Since the magnitude of the IC vector **k** decreases down to $0.002a^*$, then the light of 500 nm or smaller wavelength (i.e., with wave vector $\geqslant 0.001a^*$), should diffract in the 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) 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 an 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} and simultaneously in c_{55}, 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,[6] based on the different arguments. So, such a unique situation cannot be ignored, and understanding of its origin is of a priority importance in the quartz's phase transition problem.

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