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Comments on the characteristics of incommensurate modulation in quartz: discussion about a neutron scattering experiment

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Abstract

From analysis of the elastic neutron scattering data of Dolino *et al.* [*J. Phys. (Paris)* (1984), **45**, 361–371], it is shown that, besides the well identified components u_x and u_y of the acoustic displacements in the incommensurate (IC) phase of quartz, there also exists a strong component of the u_z vector of the modulation. The existence of the large u_z is not consistent with the currently accepted model for the IC transition in quartz, since the long-period IC modulation observed in quartz cannot induce any noticeable acoustic component u_z. The need for a new model is keenly felt in order to understand the origin of the IC modulation in quartz.

1. Introduction

The IC phase in quartz [triple-k (Dolino *et al.*, 1984) and single-k (Soula *et al.*, 1993)] exists in a small temperature range near the $\alpha \longleftrightarrow \beta$ transition and has the wavevectors of the modulation $k \simeq 0.034b$ ($b = 2\pi/a$, a is the lattice parameter) at $T_i = 850$ K, which decrease on cooling. Extensive studies have been performed on the IC phase in quartz both theoretically and experimentally as reviewed by Dolino (1986, 1990).

In the present paper, we discuss the IC structure in quartz by analyzing the elastic neutron scattering data of Dolino *et al.* (1984). It will be shown from our analysis that the IC modulation in quartz has an acoustic transversal component with amplitudes u_t and u_z (u_t is in the xy plane) of the same order of magnitude. However, as follows from the currently accepted model for this transition (Aslanyan *et al.*, 1983), the IC transition in quartz can be accompanied only by a significant u_t component, while the u_z component should be much smaller than u_t. Thus, it is necessary to develop a new model for the transition for understanding the origin of the observed IC modulation.

The discussion on the relative magnitudes of the optic and the three acoustic components in the IC modulation is also of prior importance in understanding the origin and the various properties of the IC transition. For example, since the products of the strains $u_{xz}u_{yz}$ and $u_{xy}u_{yz}$ are of the symmetry of a second-rank tensor (dielectric constant) and a component of a vector, respectively, the activity and the intensity of the modes in the Raman and the IR spectra would also be dependent upon the magnitudes of the acoustic strains. In particular, the assignment of the low-frequency Raman scattering in the IC phase (see the review by Dolino, 1986) should be based on the real structure of the IC modulation.

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2. Estimates of the u_x and u_z components

Theoretical analysis of the IC modulation in quartz and, in particular, the coupling between its optic and acoustic components was carried out by Aslanyan *et al.* (1983), and can be summarized as follows. Owing to the linear coupling between the acoustic strains in the plane perpendicular to the z axis and the gradient of the optic η mode (which is the $\alpha \longleftrightarrow \beta$ transition parameter η) of the form

$$(u_{xx} - u_{yy})\frac{\partial \eta}{\partial x} - 2u_{xy}\frac{\partial \eta}{\partial y}, \qquad (1)$$

the sinusoidal modulation of $\eta = \eta_0 \cos \mathbf{kR}$ gives rise to the modulation of strains u_{xy}, u_{xx} and u_{yy}. The strains u_{xy}, u_{xx} and u_{yy} can be represented in the form of the transversal displacement wave, $u_t \cos \mathbf{kR}$, and the longitudinal wave, $u_l \cos \mathbf{kR}$. The amplitudes of these modulations are given by the relations $u_t \simeq \eta_0 \sin \varphi$ and $u_l \simeq \eta_0 \cos \varphi$, where φ is the angle between the [110] direction of a hexagonal lattice (direction of the twofold axis which remains in the α phase) and the IC vector $\mathbf{k}$. Since the observed IC vectors in the triple-k structure almost coincide with the [100] direction (they are tilted from it by a small angle 1–7°), the modulation of the displacements in quartz is almost transversal ($\varphi \simeq 90°$ and $90 \pm 120°$). {The so called $\pm\varphi$ domains with the IC vector $\mathbf{k}$ tilted from the [100] direction by $\pm$1–7° were identified first by Gouhara & Kato (1984) in X-ray diffraction experiments.}

The u_z component of modulation was neglected in the analysis by Aslanyan *et al.* (1983) for the following reason. From symmetry considerations, it follows that

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the IC modulation in quartz can also induce the u_z component of displacements, but with a much smaller amplitude than u_t, as discussed below. Taking into account the following coupling term in the free energy expansion,

$$\left(\frac{\partial u_{xz}}{\partial y}+\frac{\partial u_{yz}}{\partial x}\right)\frac{\partial \eta}{\partial x}+\left(\frac{\partial u_{xz}}{\partial x}-\frac{\partial u_{yz}}{\partial y}\right)\frac{\partial \eta}{\partial y}, \qquad (2)$$

and substituting the modulation functions $\eta_0 \cos \mathbf{kR}$ and $u_z \sin \mathbf{kR}$ into this coupling term, one can see that it is proportional to k^3. For small k, it is significantly smaller than the coupling term, equation (1), which is proportional to k^2. [The minimization of the potential is similar to that given by Aslanyan *et al.* (1983).]

In this case, the IC modulation induces the displacement wave, $u_z \sin \mathbf{kR}$, with the amplitude $u_z \simeq k\eta_0 \sin 3\varphi$, *i.e.* $u_z \simeq k\eta_0$ for the case when the IC vector $\mathbf{k}$ is tilted from the [100] direction by a small angle $\pm(1\text{–}7^\circ)$. Since the induced u_z is proportional to the small IC wavevector k (we remind the reader that the observed IC vectors $\mathbf{k}$ are smaller or of the order of $10^{-2}b$), it should be much smaller than the amplitude u_t ($u_t \simeq \eta_0$ as pointed out above, and does not decrease as $k \to 0$). Therefore, if we accept the observed value of k, the dimensionless ratio u_z/u_t would be estimated as $u_z/u_t \simeq k/b \simeq 10^{-2}$. We shall discuss this estimate in the following section.

3. Diffraction intensity of satellites

The diffraction intensity associated with the acoustic modulation should be proportional to the square of the modulation wave amplitude. For the u_z component, this intensity should be proportional to u_z^2, or to $\eta_0^2 k^2$, and in the case of $k < 0.034b$ the contribution from u_z to the satellite intensity is expected to be $(k/b)^2 \simeq 10^{-3}\text{–}10^{-4}$ of that from u_t. Therefore, it would be too small to be observed in diffraction experiments.

Now let us compare this estimated value with those obtained by Dolino *et al.* (1984) in the elastic neutron scattering experiments. (In the following, it is shown that some satellite reflections observed in the diffraction pattern can be induced only if the IC modulation has a sufficiently large displacement component u_z, in contrast to the above expectation.)

First we note that the optic atomic displacements of η symmetry equally contribute to the scattering amplitude for all of the six satellite positions around each main Bragg reflection (see Appendix *A*). These six satellites correspond to the six orientations of the IC vector $\mathbf{k}$ in triple-k IC structure. In the case of the $h00$ Bragg reflections, it is easy to show that this contribution is originated from the optic displacements of the Si atoms in the [110] directions.

The scattering amplitude induced by the IC acoustic displacements, $\mathbf{u}(\mathbf{R})$, which also contributes to the IC satellites near Bragg reflections, is proportional to the Fourier component $\mathbf{G}+\mathbf{k}$ of the function $F_G \exp\{i\mathbf{G}[\mathbf{R}+\mathbf{u}(\mathbf{R})]\}$, where F_G is the structure factor of the lattice unit cell and $\mathbf{G}$ is the Bragg reflection vector. For the IC acoustic modulation wave of $\mathbf{u}(\mathbf{R}) = \mathbf{u}_0 \cos \mathbf{kR}$, the intensity is proportional to $(\mathbf{G}\mathbf{u}_0)^2$. In the case when the displacements amplitude $\mathbf{u}_0$ is perpendicular to the reflection vector $\mathbf{G}$, the satellite intensity would be zero. Therefore, the contribution to the IC satellite intensities from the acoustic displacements is different for different satellites around the same Bragg reflection, in contrast to that from the optic displacements, and it would be zero when $\mathbf{G} \perp \mathbf{u}_0$.

Fig. 1(*a*) [Fig. 6 in the paper by Dolino *et al.* (1984)] is the intensity map of the IC satellites around the 300 Bragg reflection in the elastic neutron scattering experiment where, instead of six satellites, only four are observed. Two satellites in that experiment are systematically extinct near each $h00$ Bragg reflection.

The systematic absence of two satellites near each $h00$ reflection means that the IC modulation in quartz is almost completely transversal acoustic [*i.e.* the longitudinal acoustic (LA) and optic components are negligibly small]. The two missing satellites correspond to the IC vectors along the direction a^* in Fig. 1(*a*) for which the transversal acoustic displacements u_t are perpendicular to the vector $\mathbf{G} = 300$.

Gouhara & Kato (1983) pointed out that the IC modulation in quartz is characterized with very small optic and LA components. However, for the extinction of the two satellites near the reflections $h00$, no explicit explanation was given by Dolino *et al.* (1984). It was interpreted as due to some symmetry considerations, which were not substantiated in that paper as discussed below in Appendix *A*.

Nevertheless, it is surprising that in the same diffraction experiment six satellites of roughly the same intensity are observed near each Bragg reflection with $h0l$ ($l \neq 0$). In Fig. 1(*b*), the IC satellites of approximately the same intensity near the reflection 022 are shown. The satellite in the position 0.03, 0, 0 near the reflection 103 is also depicted in Fig. 11 of Dolino *et al.* (1984). In these cases, the displacement vector u_t is always in the plane (001), and for the IC vector at 0.03, 0, 0 such displacements are perpendicular to the reflection vectors 022 and 103, and therefore these satellites should have zero intensity. (We note that the satellites near the reflections 103 and 022 are observed as broadened peaks even at temperatures higher than T_i.)

The only explanation for such observations can be the existence of a strong u_z component in the IC modulation. In other words, the observation of the satellite near the reflection 022 in the position 0, 0.03, 0 or near the reflection 103 in the position 0.03, 0, 0 and the absence of the satellites in the same positions near the reflection 020 or 100 is unambiguous evidence of the existence of the u_z component in the IC modulation.

Since the observed satellites have approximately the same magnitudes of intensity [see Fig. 1(b)], one should expect that the displacements u_z and u_t also have the same magnitudes. However, as mentioned before, the latter fact is not compatible with the currently accepted model of the IC transition in quartz described in the paper by Aslanyan *et al.* (1983). In other words, the softening of a mode at small k ($k = 0.035b$) and the subsequent IC transition cannot induce such a strong IC amplitude u_z. One should expect that an almost completely acoustic character of the IC modulation with u_z and u_t of the same order of magnitude must be attributed to an origin different from the generally discussed one.

4. Discussion

In their paper, Gouhara & Kato (1987) analyzed the ratio of the optic and the acoustic IC modulations from the X-ray diffraction data on the basis of the simplified model of a completely transversal acoustic modulation wave in the xy plane (only the u_t component). They found that the acoustic component is about ten times larger than the optic component. We note that the model of the completely transversal acoustic wave (without the u_z component) cannot explain the observation of six satellites of approximately the same intensity given by Dolino *et al.* (1984) for the cases such as $h0l$ ($l \neq 0$), *i.e.* near the reflection 022 (see Fig. 1b) or near the reflection 103. For the quantitative estimates, it should be taken into account that the real IC acoustic modulation in quartz always accompanies a small LA component, as mentioned above. However, the ratio $u_t/u_l \simeq \tan\varphi$ with φ in the range 90–1° and 90–7° (as given in §2) is approximately in the range between 60 and 8. If one takes into account the intensity induced by such a LA component, then it will appear that the ratio between the acoustic and the optic IC displacements estimated by Gouhara & Kato (1987) would be even larger than ten. In other words, in their model the intensity induced by the LA IC modulation (and in most cases by the u_z component) has not been taken into account, and it would have been analyzed as a contribution from the optic component.

Although the satellite intensities observed around most of the hkl reflections were semi-quantitatively explained within the accuracy of the analysis of the model presented by Gouhara & Kato (1987), they have also noticed that there are several exceptions that do not fit their model (Gouhara, 1987). In particular, near the $3\bar{3}1$ reflection, six satellites with approximately the same intensity were observed also in the X-ray diffraction as well as near the $0\bar{1}1$ reflection (see Gouhara & Kato, 1984).

The question under discussion is also related to the problem of the assignments of the phonon modes in the inelastic neutron scattering. In particular, the condition of the activity of vibrational modes in the inelastic neutron scattering can also be formulated as follows: the displacement wave induced by the vibrational mode should not be completely perpendicular to the Bragg

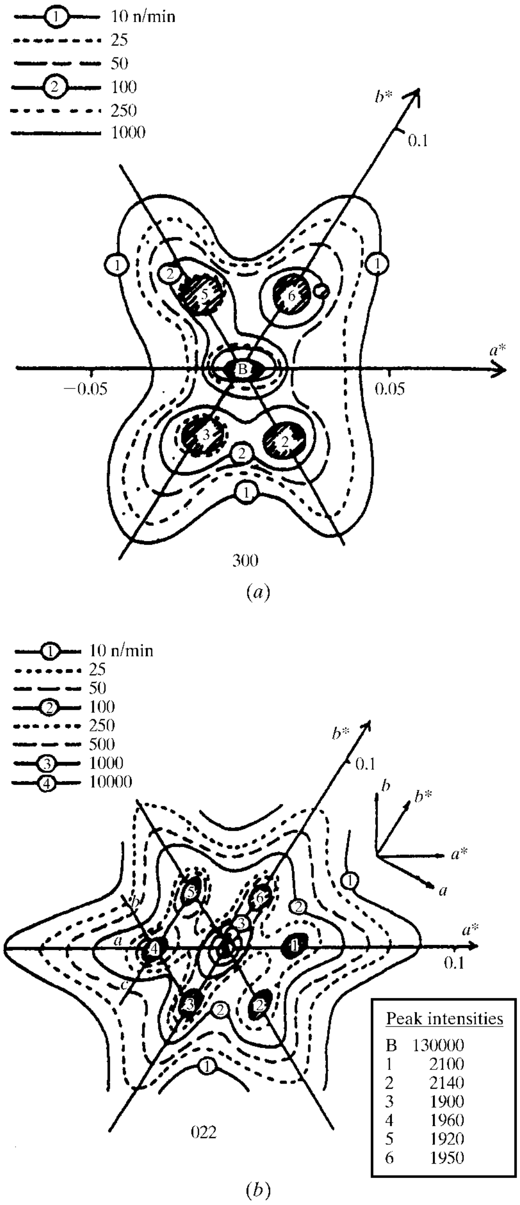

Fig. 1. (a) Four satellites observed near the reflection 300 by Dolino *et al.* (1984) in the elastic neutron scattering. Two extinct satellites in the direction a^* (parallel to the vector 300) correspond to the displacement vector u_t perpendicular to the reflection vector 300 ($|a^*| = b$ in our notations). (b) Satellite reflections near the 022 Bragg reflection in the IC phase of quartz measured in the same experiment. The six satellites have approximately the same intensity. The satellites along the vector b^* are induced by the displacement modulation component u_z.

reflection vector. From the analysis of the phonon-dispersion branches observed by the inelastic neutron scattering by Dolino *et al.* (1992) the softening of some mode at $k \simeq 0.035b$ on cooling from the β to the IC phase was obtained. In the context of the present paper, we think that their analysis should be revised because the fact that the transversal acoustic mode u_z at small $k = 0.035b$ (which is denoted in that paper as TA_2) is not active in their neutron scattering experiment (u_z is perpendicular to the Bragg reflection vector 110) has not been taken into account. The existence of the strong u_z component in the IC modulation, as follows from the above development, does not contribute to the elastic neutron scattering in the (001) plane. This fact proves that the acoustic phonon u_z with the same wavevector $k \simeq 0.035b$ also does not contribute to the scattering in the same (001) plane in the inelastic scattering.

We note the following observation, which also cannot be fully understood in the frame of the existing model for the IC transition in quartz. The soft optic η mode in quartz is Raman inactive in the high-temperature β phase. The strains u_{xy} applied to the crystal (or existing in the crystal) cannot make this mode Raman active. According to Gouhara & Kato (1983, 1987), as discussed above, the IC phase of quartz is almost purely an acoustic modulation, with a very small optic component. Therefore, such IC modulation cannot make the η mode active in the Raman scattering with normal intensity. Then, a question arises on the origin of the overdamped Raman peak observed in the IC phase. It has an intensity typical of an optic mode, and is observed even above T_i with the same order of intensity (see, for example, Dolino, 1986).

In conclusion, it was shown that the IC phase of quartz has a strong u_z acoustic component of modulation. The strong u_z component and the dominating acoustic character of the IC modulation should be added to other anomalous observations near the $\alpha \longleftrightarrow \beta$ transition, such as the macroscopic inhomogeneous structure, the anomalous light scattering, the transversal acoustic anomalies and the birefringence along the z direction. All these anomalies have not been interpreted yet in the frame of the currently accepted model for the transition in quartz. It should be added that recently a new interpretation of these anomalies has been developed by the present authors [see Aslanyan (1998*a*,*b*) and Shigenari *et al.* (1998)].

APPENDIX *A*

We shall demonstrate here that all the six satellites should have the same intensities around any Bragg reflection if they originate from the optic component of the IC modulation. Therefore, the extinction of some satellites among the six is not a consequence of symmetry, as is assumed by Dolino *et al.* (1984). The following calculations of the scattering amplitude are based on the work of Krivoglaz (1996).

One should introduce the electron-density wave for the lattice unit cells, $F_G \exp\{i\mathbf{G}[\mathbf{R} + \mathbf{u}(\mathbf{R})]\}$, where vector $\mathbf{R}$ gives the position of the unit cell in the undistorted crystal, $\mathbf{u}(\mathbf{R})$ is the acoustic IC displacements vector and F_G is the structure factor of the unit cell, which depends on the optic atomic displacements. Now F_G is presented as an expansion, $F_G = F_G^0 + \gamma_G \eta$ (where F_G^0 is the structure factor of the undistorted unit cell and γ_G is the coefficient of the expansion). This expression shows that the optic atomic displacements enter into F_G only through the parameter η. Since the IC modulation function $\eta(R)$ for the triple-k structure is given by $\eta_0(\cos \mathbf{k}_1\mathbf{R} + \cos \mathbf{k}_2\mathbf{R} + \sin \mathbf{k}_3\mathbf{R})$, the corresponding electron-density wave is given by

$$F_G^0 \exp\{i\mathbf{G}[\mathbf{R} + \mathbf{u}(\mathbf{R})]\} + \gamma_\mathbf{G}\eta_0\{\exp[i(\mathbf{G} \pm \mathbf{k}_1)\mathbf{R}] + \exp[i(\mathbf{G} \pm \mathbf{k}_2)\mathbf{R}] \pm i \exp[i(\mathbf{G} \pm \mathbf{k}_3)\mathbf{R}]\}.$$

For calculating the scattering amplitude, one should take a Fourier component of this expression. It is easy to see that the scattering amplitude induced by the optic modulation η has the same modulus ($|\gamma_G \eta_0|$) for all six scattering vectors, $\mathbf{Q} = \mathbf{G} \pm \mathbf{k}_1$, $\mathbf{Q} = \mathbf{G} \pm \mathbf{k}_2$ and $\mathbf{Q} = \mathbf{G} \pm \mathbf{k}_3$.

This is quite a general argument. Thus, we do not agree with the symmetry arguments of Dolino *et al.* (1984), in order to interpret the extinction of some satellites among the six. Such an extinction can only be a consequence of a transversal acoustic IC modulation in quartz accompanied by the extremely small optic and LA components, as shown by Gouhara & Kato (1983), and also pointed out in this paper.

The authors thank Professor N. Kato for valuable discussions. It should be added, however, that Professor N. Kato considers that the observations in elastic neutron scattering by Dolino *et al.* (1984) are not completely compatible with the X-ray observations by Gouhara & Kato (1983).

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