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# On the origin of the inhomogeneities and birefringence in the incommensurate phase of quartz

T A Aslanyan<sup>†</sup>, T Shigenari and K Abe

Department of Applied Physics and Chemistry, University of Electro-Communications, Chofu-shi, Tokyo 182, Japan

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**Abstract.** It is shown that the incommensurate (IC) phase near the  $\alpha \leftrightarrow \beta$  transition point in quartz ( $\text{SiO}_2$ ) is an improper ferroelastic one and should be split into domains. The birefringence induced by such a ferroelastic phase is estimated, and it is shown that it can be as strong as is observed in experiments only if one accepts a new model for the IC transition in quartz.

## 1. Introduction

The incommensurate (IC) phase in quartz (triple- $k$  [1] and single- $k$  [2] phases) exists over a small temperature range near the  $\alpha \leftrightarrow \beta$  transition and has a modulation period corresponding to the wavevectors  $k \sim 10^{-2}\mathbf{b}$  ( $\mathbf{b}$  is the reciprocal-lattice vector), which decreases on cooling. One of the peculiarities of the IC phase in quartz is the macroscopic inhomogeneous structure observed in various optical and electron microscopy experiments [1, 3, 6, 10], which lies at the origin of the anomalous light scattering in quartz [5–11]. For the same temperature range as that over which the IC ‘hexagonal’ phase exists, in quartz, strong birefringence ( $\epsilon_{xx} - \epsilon_{yy} \sim 10^{-5}$ ) [10, 16–18] of the light propagating in the  $z$ -direction was observed, which unambiguously indicates that the IC phase is ferroelastic. Other explanations of the observed birefringence (such as temperature gradients, or an idea advocated by Dolino [8] of mixing of  $\alpha$ - and  $\beta$ -phases) are commented on below and shown to be unacceptable.

The inhomogeneities appearing near the transition temperature were identified subsequently (van Tendeloo *et al* [1]) as domains of the IC phase. The existence of inhomogeneities (domains) is an inevitable consequence of the ferroelastic and ferroelectric phase transitions and is a well studied phenomenon for these crystals. In the present paper it is shown that the IC phase of quartz is an improper ferroelastic one in view of its symmetry, and therefore should be split into domains. Elastic strains induced by the IC modulation are proportional to the square of the IC amplitude and the square of the IC wavevector’s components.

Ferroelasticity in the IC phase of quartz was discussed also in a paper by Saint-Gregoire *et al* [12]. However, we do not agree that the effect described in that paper can be accepted as ferroelasticity, and this is commented on below.

Light scattering from the ferroelastic domain walls in the IC phase of quartz, the polarization properties of the scattered light, the transverse acoustic anomalies of the

<sup>†</sup> Permanent address: Institute for Physical Research, Armenian National Academy of Sciences, Ashtarak-2, 378410 Armenia.

ferroelastic phase and some other consequences of the ferroelasticity were briefly discussed by the present authors in references [13] and [14] (a more detailed consideration of them will be published elsewhere).

Our estimates of the ferroelastic effect (calculated below) indicate that it would be very small for the observed long-period IC structure (it is proportional to the square of the small IC vector,  $k^2$ ). This effect could be large and exactly fit the observed magnitude of the birefringence (and also the light scattering and acoustic anomalies [13]) if the IC structure of quartz had a short period (if the IC vector was of the order of the reciprocal-lattice vector  $b$ ). The main anomalies observed for quartz can be easily explained if one assumes that the observed long-period IC structure is the third harmonic of a short-period structure with a structure vector close to  $b/3$  (i.e., equal to  $b/3 + \kappa$ , where  $\kappa$  is small, while the observed IC vector  $k = 3\kappa$ ) and that the short-period IC modulation are strongly attenuated by the Debye–Waller factor and are thus not observed in experiments.

The Debye–Waller factors for the IC structures have been calculated by the present authors [19], and it has been shown that they should be very small in the immediate vicinities of displacive-type IC transitions, which can lead to the IC satellites not being observable in diffraction experiments. In our paper [19], we also discussed earlier calculations of the Debye–Waller factors for the IC structures carried out by Overhauser [20] and by Axe [21]. The situation in which the IC third-harmonic modulation amplitude is larger than the amplitude of the fundamental modulation  $b/3 + \kappa$  has been also discussed by the present authors [22]. It was shown [22] that such a situation directly follows from the Landau theory near the lock-in transition, when  $\kappa \rightarrow 0$ , and that the amplitude of the third-harmonic modulation increases as  $\kappa^{-1}$ . More detailed analysis of the above-described situation will be published elsewhere.

## 2. Ferroelasticity in the IC phase

In this section we show that as a result of the IC phase transition in the crystal, equilibrium strains appear and form ferroelastic domain structures in both the single- and the triple- $k$  IC phases. Since our consideration is based mainly on the symmetry properties of the IC phase, our procedures for estimating the strains and other quantities induced by strains will be carried out for the cases of small and large IC wavevectors.

The starting point of our consideration is the expansion of the thermodynamic potential as a function of the order parameter  $\eta$ , its space derivatives and the elastic strains:

$$\begin{aligned} \Phi = \int dR \left\{ \Phi_0 + \frac{\alpha}{2}\eta^2 + \frac{g}{2}(\nabla\eta)^2 + \frac{g_1}{4}(\nabla^2\eta)^2 + \frac{B}{4}\eta^4 + r\eta^2 u_{11} + \frac{c_{11} - c_{66}}{2}(u_{11} + u_{22})^2 \right. \\ \left. + \frac{c_{66}}{2}[(u_{11} - u_{22})^2 + 4u_{12}^2] + a \left[ \frac{\partial\eta}{\partial x}(u_{11} - u_{22}) - 2\frac{\partial\eta}{\partial y}u_{12} \right] \right. \\ \left. + r_1 \left[ \left( \left( \frac{\partial\eta}{\partial x} \right)^2 - \left( \frac{\partial\eta}{\partial y} \right)^2 \right) (u_{11} - u_{22}) + 4\frac{\partial\eta}{\partial x} \frac{\partial\eta}{\partial y} u_{12} \right] \right\}. \end{aligned} \quad (2.1)$$

A potential of this type was analysed in reference [15]. We now go on to write down the expressions for potential (2.1) corresponding to the single- $k$  IC structure with

$$\eta(R) = \sqrt{2}\rho \cos(\mathbf{k} \cdot \mathbf{R} + \varphi)$$

and the triple- $k$  IC structure with

$$\eta(R) = \sqrt{2}\rho_1 \cos(\mathbf{k}_1 \cdot \mathbf{R} + \varphi_1) + \sqrt{2}\rho_2 \cos(\mathbf{k}_2 \cdot \mathbf{R} + \varphi_2) + \sqrt{2}\rho_3 \cos(\mathbf{k}_3 \cdot \mathbf{R} + \varphi_3)$$

where  $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$ .

2.1. The single- $\mathbf{k}$  IC phase and its ferroelastic domains

Substituting  $\eta(R)$  into equation (2.1), one obtains after minimization with respect to the elastic displacements  $\mathbf{u}_k$  ( $\mathbf{k}$  is the wavevector of the IC structure) the expression for the potential of the single- $\mathbf{k}$  IC phase:

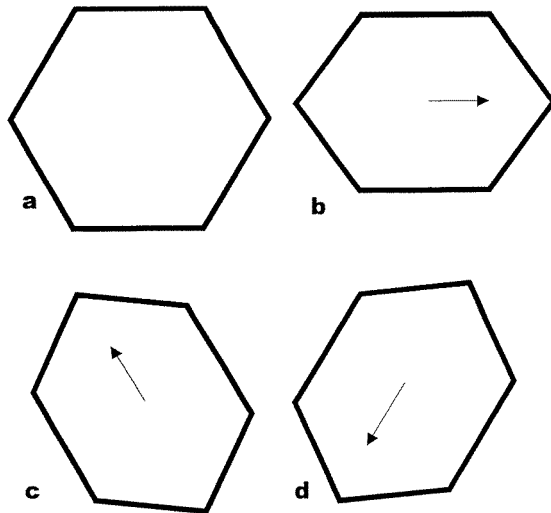
$$\Phi_{1k} = \frac{\tilde{\alpha}}{2}\rho^2 + \left(\frac{3B}{8} - \frac{r^2}{2c_{11}}\right)\rho^4 + r_1k^2\rho^2[(u_{11} - u_{22})\cos 2\phi + 2u_{12}\sin 2\phi] + \frac{c_{11} - c_{66}}{2}(u_{11} + u_{22})^2 + \frac{c_{66}}{2}[(u_{11} - u_{22})^2 + 4u_{12}^2] \quad (2.2)$$

where  $\phi$  is the angle between the  $x$ -axis and the IC wavevector, and the coefficient  $\tilde{\alpha}$  is

$$\tilde{\alpha} = \alpha + \frac{1}{2}\left(g - \frac{a^2 \cos^2 3\phi}{c_{11}} - \frac{a^2 \sin^2 3\phi}{c_{66}}\right)k^2 + \frac{g_1k^4}{4}.$$

As was shown in reference [14] and as follows directly from equation (2.2), the equilibrium values of  $\phi$  are  $\phi = \pi/2, \pi/2 \pm 2\pi/3$ , and they coincide with the symmetry axes of the crystal. The equilibrium values of  $u_{11} - u_{22}$  and  $u_{12}$  can be obtained by the appropriate minimization of equation (2.2), and are

$$\begin{aligned} (1) \quad \bar{u}_{12} &= 0 & \bar{u}_{11} - \bar{u}_{22} &= -\frac{r_1\rho^2k^2}{c_{66}} \\ (2) \quad \bar{u}_{12} &= -\frac{\sqrt{3}r_1\rho^2k^2}{2c_{66}} & \bar{u}_{11} - \bar{u}_{22} &= \frac{r_1\rho^2k^2}{2c_{66}} \\ (3) \quad \bar{u}_{12} &= \frac{\sqrt{3}r_1\rho^2k^2}{2c_{66}} & \bar{u}_{11} - \bar{u}_{22} &= \frac{r_1\rho^2k^2}{2c_{66}}. \end{aligned} \quad (2.3)$$



**Figure 1.** Ferroelastic distortions of the crystal's hexagonal lattice cell (a) in the IC phase of quartz. The arrows depict the orientations of the IC wavevectors in the three domains, (b), (c), (d), of the single- $\mathbf{k}$  IC structure corresponding to the three solutions of equation (2.3)

So, we have revealed that the single- $\mathbf{k}$  phase of quartz is an improper ferroelastic one (the elastic strains are proportional to the square of the order parameter  $\rho^2$ ), with three types

of domain given by equation (2.3). The distortions of the crystal's hexagonal lattice cell for the cases of the three orientations of the IC wavevector are depicted in figure 1. Domains with such IC wavevectors were observed in diffraction experiments [2]. We note that the crystal should be split into the domains of equation (2.3) for any values of  $k$ ; this includes the case of the commensurate single- $k$  lock-in phase with vector  $\mathbf{k} = \mathbf{b}/3$ .

Our general consideration of the ferroelastic domain formation is as follows [23]. Nucleation of any of the several types of domain of equation (2.3) as a result of the IC phase transition will induce strains not only in the same domain but also in some adjacent range of the crystal having a volume of the same order as that of the domain. A corresponding positive contribution to the thermodynamic potential should therefore be added to equation (2.2). Since  $\bar{u}_{11} - \bar{u}_{22}$  and  $\bar{u}_{12}$  are proportional to  $\rho^2 k^2$ , this contribution, being of the same order of magnitude as the volume, is proportional to  $\rho^4 k^4$ . To avoid such a loss in the thermodynamic potential, the formation of the IC structure caused by the phase transition should take place simultaneously in the three domains (1), (2) and (3) of equation (2.3), making the space-averaged strains  $u_{11} - u_{22}$  and  $u_{12}$  equal to zero. The loss in the thermodynamic potential in such a case will be of the same order of magnitude as the surface, and hence negligibly small. The domains in such a case involve distortions of the lattice cells like those shown in figure 1 and should take the form of columns parallel to the  $z$ -axis. It is generally the case that the components of the strains are proportional to the square of the IC structure amplitude (and hence are non-zero) for all IC phases, because of the existence of terms similar to that with the coefficient  $r_1$  in equation (2.1). However, in the case of quartz symmetry, there are available different directions of IC modulation and, as a result of this, complete compensation of elastic strains of the above type becomes possible. The domains with strains given by equation (2.3) (with distortions as in figure 1) should take the form of columns elongated in a direction parallel to the  $z$ -axis.

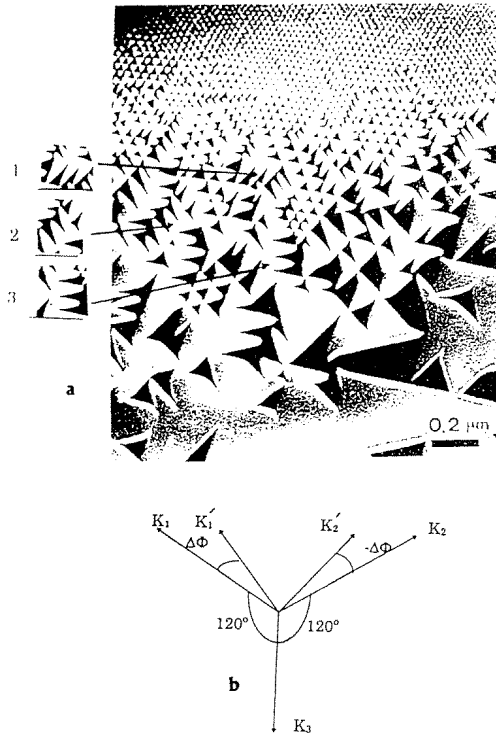
## 2.2. The triple- $k$ phase

Let us consider now the situation with triple- $k$  IC structure. We show that again the phase should be split into ferroelastic domains. The expression for the thermodynamic potential takes the form

$$\begin{aligned} \Phi_{3k} = & \sum_{i=1}^3 \frac{\tilde{\alpha}}{2} \rho_i^2 + \left[ \frac{45B}{8} - \frac{3r^2}{2c_{11}} \right] \left( \sum_{i=1}^3 \rho_i^2 \right)^2 + r_1 \sum_{i=1}^3 [\rho_i^2 k_i^2 (u_{11} - u_{22}) \cos 2\phi_i \\ & + 2k_i^2 \rho_i^2 u_{12} \sin 2\phi_i] + \frac{c_{11} - c_{66}}{2} u_{11}^2 + \frac{c_{66}}{2} [(u_{11} - u_{22})^2 + 4u_{12}^2] \end{aligned} \quad (2.4)$$

where the  $\phi_i$  ( $i = 1, 2, 3$ ) are the angles between the wavevectors  $\mathbf{k}_1$ ,  $\mathbf{k}_2$ ,  $\mathbf{k}_3$  of the IC structure and the  $x$ -axis respectively. In equation (2.4), some higher-order terms have been omitted since they are not important for the problem in question. In the regular triple- $k$  structure where  $k_1 = k_2 = k_3$ ,  $\rho_1 = \rho_2 = \rho_3 = \rho$  and the angles  $\phi_1, \phi_2, \phi_3$  differ from each other by  $2\pi/3$ , the term with the coefficient  $r_1$  in equation (2.4) is equal to zero and therefore it cannot induce strains. In other words, each plane wave of the triple- $k$  structure induces strains, similar to those of equation (2.3), but the sum of these strains is equal to zero in the case of the regular triple- $k$  structure. The situation becomes completely different in the irregular triple- $k$  structure.

Figure 2(a) shows the electron microscopy dark-field image of the IC structure of quartz obtained by Yamamoto *et al* [4]. A similar pattern for the IC structure was obtained by van Landuyt *et al* [3]. The upper part of figure 2(a) corresponds to the high-temperature range of the triple- $k$  structure, which is composed of equilateral (regular) triangles (at least, within



**Figure 2.** (a) An electron microscopy dark-field image of the IC structure of quartz observed by Yamamoto *et al* [4]. The bottom part of the figure with irregular elongated triangles corresponds to the low-temperature range of the IC structure. 1, 2 and 3 are the ferroelastic domains shown by the arrows in the crystal. The domains 1, 2 and 3 are tilted with respect to each other by exactly  $120^\circ$ . (b) The IC vectors of the triple- $k$  structure corresponding to the regular (equilateral) triangles:  $k_1, k_2, k_3$ , and irregular (not equilateral) triangles:  $k'_1, k'_2, k'_3$ .

the accuracy of figure 2(a) they can be considered as a regular). The lower part of figure 2(a) corresponds to the low-temperature range and is composed of significantly irregular triangles. In the  $\gamma$ -ray experiment carried out by Bastie and Dolino [25] the diffraction from this pattern was observed (i.e., the IC satellites were resolved) down to  $k = 0.005b$ , i.e., up to sizes of the triangles of  $\approx 100$  nm (the middle part of figure 2(a)). One can see the growth of the distortions (elongation) of the equilateral triangles with the decrease of temperature from the upper to the lower part of figure 2(a).

The most striking peculiarity of the ‘irregular’ triangles in figure 2(a) is that the orientation of the directions of their elongation in different parts of figure 2(a) (i.e., in different parts of the crystal), which are denoted as 1, 2 and 3 and are shown by the arrows, are strongly correlated. The directions of the orientations of areas 1, 2, 3 in figure 2(a) are tilted with respect to each other by exactly  $60^\circ$  (or  $-120^\circ$ ).

This means that the observed irregularities are not induced by temperature gradients or other external factors, but are of intrinsic nature. The intrinsic (equilibrium) nature of the observed irregular triangles was emphasized also by Saint-Gregoire *et al* [12], who observed the lack of correlation between the temperature gradients and the orientations of the triangles in an electron microscopy experiment.

The equilibrium nature of the irregularities can also be seen from the following

consideration. The equilateral triangles observed near the  $\beta$ -phase become elongated on cooling, and such a distortion in terms of the IC wavevectors is shown in figure 2(b) (the IC vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$  are tilted to take up the directions  $\mathbf{k}'_1$  and  $\mathbf{k}'_2$  respectively, and their lengths are also changed). The magnitude of the distortion can be characterized by the angle  $\Delta\phi$  in figure 2(b), or by the difference  $k_1^2 - k_1'^2$  or  $k_2^2 - k_2'^2$  in figure 2(b). Since under the conditions of the experiments the temperature gradients are not larger than  $1 \text{ K cm}^{-1}$ , the sizes of the irregular triangles in figure 2 are of the order of 100 nm; therefore the temperature difference over the area of each triangle is estimated to be less than  $10^{-5} \text{ K}$  and this cannot induce any measurable distortion of the IC lattice cell.

Due to such irregularity of the triple- $\mathbf{k}$  structure, the term with coefficient  $r_1$  in equation (2.4) becomes non-zero and, as can be obtained from the minimization of the potential (2.4), the strains in such a case are also proportional to the square of the IC amplitude  $\rho^2$  and to the square of the IC wavevectors' components, as in the case of the single- $\mathbf{k}$  IC structure.

To consider the symmetry properties of possible domain structures in the irregular triple- $\mathbf{k}$  phase, we shall use the following simplified description. The irregular triple- $\mathbf{k}$  structure can be introduced as a structure with IC wavevectors  $\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3 = 0$  making angles  $\phi_1 + \Delta\phi$ ,  $\phi_2 - \Delta\phi$  and  $\phi_3$ , where  $\phi_2 - \phi_1 = \phi_3 - \phi_2 = 2\pi/3$  and  $\rho_1 = \rho_2 = \rho_3$ . In other words, the structure vectors of such a phase are tilted from their regular positions by the angle  $\Delta\phi$  (see figure 2(b)) and the corresponding IC modulation makes a pattern of significantly elongated triangles in the case of large distortion angle  $\Delta\phi$ . Expanding the term with the coefficient  $r_1$  in (2.4) in terms of  $\Delta\phi$ , one obtains

$$r_1 k^2 \rho^2 [(\sqrt{3} \sin 2\phi_1 + \cos 2\phi_1)(u_{22} - u_{11}) + 2(\sqrt{3} \cos 2\phi_1 - \sin 2\phi_1)u_{12}] \Delta\phi \quad (2.5)$$

where  $k$  has the magnitude of the IC wavevectors. (We have used above an expansion in terms of  $\Delta\phi$  so as to keep our expressions simple, but the same result can be easily obtained directly, without recourse to such an expansion.) The symmetry properties of this term are the same in the cases of small and large values of  $\Delta\phi$  (small and large irregularities). Minimizing the potential (2.4) with respect to  $u_{11} - u_{22}$  and  $u_{12}$ , one obtains for domain (1)

$$\begin{aligned} \bar{u}_{11} - \bar{u}_{22} &\sim \frac{r_1 k^2 \rho^2 \Delta\phi}{c_{66}} (\sqrt{3} \sin 2\phi_1 + \cos 2\phi_1) \\ \bar{u}_{12} &\sim -\frac{r_1 k^2 \rho^2 \Delta\phi}{c_{66}} (\sqrt{3} \cos 2\phi_1 + \sin 2\phi_1) \end{aligned} \quad (2.6a)$$

and for domains (2) and (3)

$$\begin{aligned} \bar{u}_{11} - \bar{u}_{22} &\sim \frac{r_1 k^2 \rho^2 \Delta\phi}{c_{66}} \left[ \sqrt{3} \sin\left(2\phi_1 \pm \frac{2\pi}{3}\right) + \cos\left(2\phi_1 \pm \frac{2\pi}{3}\right) \right] \\ \bar{u}_{12} &\sim -\frac{r_1 k^2 \rho^2 \Delta\phi}{c_{66}} \left[ \sqrt{3} \cos\left(2\phi_1 \pm \frac{2\pi}{3}\right) + \sin\left(2\phi_1 \pm \frac{2\pi}{3}\right) \right] \end{aligned} \quad (2.6b)$$

where the signs  $\pm$  correspond to the domains (2) and (3) respectively. So, we have established that the irregular triple- $\mathbf{k}$  IC structure has the same energy for three orientations of such a structure rotated with respect to each other by the angles  $\pm 2\pi/3$  and that it induces strains, which are different (solutions (1), (2) and (3) of equations (2.6)) for different orientations. The sum of the  $\bar{u}_{11} - \bar{u}_{22}$  (and the  $\bar{u}_{12}$ ) given by the solutions (1), (2) and (3) is equal to zero. This means that the spatially averaged strains induced by three adjacent domains of equal volumes are zero, which is necessary for ferroelastic domain structure formation. These domains should have the form of columns elongated in

a direction parallel to the  $z$ -axis. The elongated triangles have three different orientations in the three domains of equations (2.6).

In figure 2(a) one can distinctly observe areas (denoted as 1, 2, 3) composed of groups of irregular triangles with the same orientations. We identify each such area, having a consistent orientation of the triangles in it, with a ferroelastic domain (i.e., 1, 2, 3 are three ferroelastic domains).

Each of the domains given by equations (2.6) can be split also into rotation domains with different angles  $\pm\phi_i$ . As can be directly seen from equation (2.4), the simultaneous replacement of the angles  $\phi_i$  by  $-\phi_i$  and of  $u_{12}$  by  $-u_{12}$  does not change the potential (2.4). The angles  $\pm\phi_i$  correspond to the so-called rotation domains of the triple- $\mathbf{k}$  IC structure and have been observed in various experiments [2, 11, 24]. The strains  $u_{12}$  induced in such domains have different signs, and the averaged strains  $u_{12}$  in two adjacent domains are cancelled in the case of equal volumes of such domains. But the components of the strains  $u_{11} - u_{22}$  do not change upon the replacement of  $\phi_i$  by  $-\phi_i$ , have the same sign in different domains and are not cancelled. So, for such domains only partial compensation of the averaged strains takes place, but even such partial compensation makes the formation of such domain structure favourable.

The rotation domains were observed in electron microscopy, x-ray and neutron diffraction experiments also for the regular triple- $\mathbf{k}$  structure [2, 3, 11], which is not ferroelastic according to the above consideration. However, we note that a more precise method for determining whether the triple- $\mathbf{k}$  structure observed in the high-temperature range (the upper part of figure 2(a)) is regular or not is that of the measurement of the birefringence for light propagation in the  $z$ -direction.

Now we shall discuss the effect of ferroelasticity described by Saint-Gregoire *et al* [12]. In the paper [12] it is claimed that, due to the interaction between the domain walls separating the triangles depicted in figure 2(a), each triangle acquires equilibrium non-zero strain, and therefore the IC phase can be considered as a ferroelastic one. However, we do not agree that such an effect can be considered as ferroelasticity. Each triangle depicted in figure 2(a) is only a part of the long-period IC lattice cell (six adjacent triangles make up the lattice cell of the triple- $\mathbf{k}$  IC structure). Since any IC structure always induces an IC wave of acoustic displacements, a part of the IC lattice cell (i.e., a part of the IC period) always acquires equilibrium non-zero strains. However, the spatial average of such strains over the IC period is, in general, zero, and therefore the effect discussed by Saint-Gregoire *et al* [12] cannot be considered as ferroelasticity. In other words, each triangle in figure 2(a) was identified as a ferroelastic domain [12], while each such triangle is only a part of the IC period. Ferroelasticity appears only in the case in which the IC lattice cell acquires non-zero strains as a whole (i.e., the sum of the strains induced by the six adjacent triangles in figure 2(a) is non-zero); this possibility is introduced in the present paper. Also, in the paper [12], the magnitude of the effect is not estimated, and it is not made clear whether it is an observable effect or not.

### 3. Discussion

Since the dielectric constant's components are of the same symmetry as the strains and are proportional to the strain's components, for the ferroelastic structure  $\epsilon_{xx} - \epsilon_{yy} \simeq 10^{-1}(\bar{u}_{xx} - \bar{u}_{yy})$  and  $\epsilon_{12} \simeq 10^{-1}\bar{u}_{12}$  ( $10^{-1}$  is the order of magnitude of the corresponding optical-mechanical coefficient of quartz) and thus the crystal in the IC phase should acquire birefringence for light propagating in the  $z$ -direction. Such a birefringence was observed in quartz [10, 16–18], and for  $\epsilon_{xx} - \epsilon_{yy}$  the value  $5 \times 10^{-5}$  was measured [10]. The observed



birefringence was explained in reference [10] as an effect induced by the temperature gradients in the crystal. We assert that the temperature gradients cannot induce in the case of quartz symmetry any birefringence, since

$$\epsilon_{xx} - \epsilon_{yy} \sim \frac{\partial^2 T}{\partial x^2} - \frac{\partial^2 T}{\partial y^2}$$

which is zero in the case of linear temperature gradients. Other kinds of coordinate dependency of the temperature (e.g.  $T \sim x^2$  or  $x^3$ ) are extremely unlikely and can give only negligibly small contributions to the birefringence.

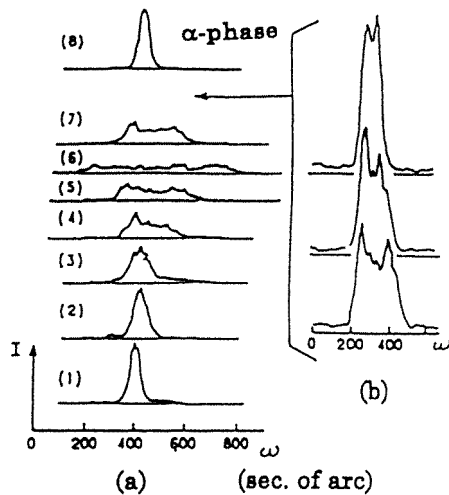
To estimate the magnitude of the birefringence induced by the strains, one should estimate the values of the strains in the IC structure. The magnitudes of the strains  $\bar{u}_{11} - \bar{u}_{22}$  and  $\bar{u}_{12}$  of equations (2.3), (2.6) can be estimated by taking into account the fact that the IC modulation amplitude  $\rho \sim \sqrt{-\tilde{\alpha}/B}$  within 1 K ( $1 \text{ K} \sim 10^{-4} T_{at}$ ) of the transition temperature takes the value  $10^{-2} \rho_{at}$  ( $T_{at}$  is the atomic temperature and  $\rho_{at}$  is the amplitude of an IC modulation with displacements of the atomic order of magnitude). The IC wavevector in relations (2.3), (2.6) according to observations in diffraction experiments is of the order of  $\sim 10^{-2} b$  ( $b$  is the reciprocal-lattice vector) and tends to zero on cooling. Assuming that the remaining coefficients in (2.3), (2.6) are of the atomic order of magnitude for the dimensionless strains  $u_{11} - u_{22}$  and  $u_{12}$ , one obtains an estimate of at most  $\sim 10^{-7} - 10^{-8}$ , which gives for  $\epsilon_{xx} - \epsilon_{yy}$  a magnitude of  $10^{-8} - 10^{-9}$  or less. This magnitude is much less than what would be required to induce the strong birefringence which is observed in the experiments. The birefringence observed in the experiments could be expected only if the IC structure had a much shorter period (larger IC wavevectors).

For the case of large IC wavevectors ( $k \simeq b/3$  according to our assumption), similar estimation gives for the strains  $\bar{u}_{11} - \bar{u}_{22}$  and  $\bar{u}_{12}$  the order of magnitude  $\sim 10^{-4}$ , and consequently for  $\epsilon_{xx} - \epsilon_{yy}$  the value  $\sim 10^{-5}$ , which is completely consistent with the experimental observations [16, 17, 10, 18]. For the triple- $k$  IC structure, such an order of magnitude is obtained only in the case of strong irregularities (e.g., in the case of large angles  $\Delta\phi$  in equation (2.6)).

We note that, according to Bachheimer [18] and our recent observations, the birefringence is observed in the temperature range of the single- $k$  IC structure and in the low-temperature range of the triple- $k$  structure (i.e., in the temperature range where the triple- $k$  structure is strongly irregular). Also, according to our assumption, in the low-temperature range of the triple- $k$  structure a lock-in transition to the phase with structure vector  $b/3$  is expected. Such a lock-in phase should also be ferroelastic, like the single- $k$  IC structure. The observation of the peaks of the birefringence in both temperature ranges [18] is completely consistent with our model, although we think that more accurate measurements are needed to determine whether the triple- $k$  IC structure is irregular over the whole temperature range, or only at lower temperatures.

So, we have revealed that the birefringence induced by the IC phase in quartz differs by factors of  $10^3 - 10^4$  between the cases of the observed small and the assumed large IC wavevectors. This should be considered as one of the main confirmations of our assumption regarding the existence in quartz of the 'invisible' short-period IC structure (i.e. structure that cannot be directly observed as a satellite).

In our interpretation, the 'fog' zone in quartz (the temperature range just above the  $\alpha$ -phase, i.e., between the curves (7) and (8) in figure 3) is the lock-in phase with the structure vector  $b/3$ . It should be emphasized that in the  $\gamma$ -ray diffraction [25] the IC satellite reflections were not observed in the 'fog' zone (they merged into the main Bragg reflection). The assumption that the 'fog' phase is not incommensurate, but is the structure with vector



**Figure 3.** (a) The variation of the shape of the (2 2 0) Bragg peak in the temperature range extending from that of the IC phase to that of the  $\alpha$ -phase (curves (1)–(8)) obtained by means of  $\gamma$ -ray diffraction by Bastie and Dolino [25]. The satellite reflections were observed near the Bragg peak down to  $0.005b$  (i.e., for sizes of the triangles up to  $\approx 100$  nm, observed in the middle part of figure 2(a)), and afterwards had merged into it. (b) The same peak in the temperature range between curves (7) and (8) (adjacent to the  $\alpha$ -phase, in the so-called fog zone). In that range the IC satellites are absent and the peak has a two-peak structure typical for the ferroelastic crystal. The sharpness of the split peaks is a manifestation of very homogeneous strains in the crystal.

$b/3$ , is confirmed also by the observed [7] generation of the second harmonic of light in the same temperature range. Also, it can explain why the strong first-order transition from the IC to the  $\alpha$ -phase occurs, since, for the observed long-period IC structure with  $k \rightarrow 0$ , on approaching the  $\alpha$ -phase upon cooling an almost continuous transition is expected.

We shall now discuss the model of the coexistence (mixture) of the  $\alpha$ - and  $\beta$ - (or IC) phases proposed by Dolino [8] as explaining the light scattering in quartz. This model was denied by Shustin *et al* [9] and Yakovlev and Shustin [10]. Since the dielectric constant difference between adjacent  $\alpha$ - and  $\beta$ -domains takes the value  $10^{-3}$ , in such a case the crystal would not be transparent to light. We can add to these arguments that the enormous scattered intensity in such a case should be almost completely polarized regardless of the crystal's orientation (since the dielectric constant differs mainly in its diagonal components in adjacent domains), while in the experiment carried out by Dolino [8] the completely polarized scattered light changes to completely depolarized light upon rotation of the crystal about the  $z$ -axis. So, the model of the mixture of the phases can explain neither the observed intensity of the scattered light, nor its polarization properties. We note that in the paper by Dolino [8] the intensity of the scattered light for the model under consideration was not estimated and the compatibility of the observed polarization properties with those following from the model was not discussed.

The model of the mixture of phases was denied also by Gouhara and Kato [24]. In x-ray topography studies of the IC phase of quartz, they directly observed the *absence* of such states. The mixture of phases was also not identified in various electron microscopy studies of the IC phase of quartz.

A typical ferroelastic splitting of the (2 2 0) Bragg reflection in the  $\gamma$ -ray diffraction

experiment by Bastie and Dolino [25] (see figure 3) in the temperature range of the ‘fog’ zone was interpreted as an effect induced by the coexisting mixed phases. It should be noted that the observed sharpness of the split peaks [25] (see figure 3(b)) proves that they are induced by homogeneously spatially distributed strains (as they should be in ferroelastics) and not by the irregular distortions induced by the mixed phases. (In irregularly distorted crystals, only a broadening of the Bragg reflections is expected, and not a splitting.) The magnitude of the birefringence can be estimated also from the splitting of the Bragg reflection in figure 3. The angular position of the split reflection is given by  $\mathbf{G} + \Delta\mathbf{k}$  ( $\mathbf{G}$  is the (2 2 0) reflection vector), and  $\Delta k/G \sim \sin \Delta\alpha$ , where  $\Delta\alpha \sim 100''$  (seconds of arc) (see figure 3). Taking into account that  $\bar{u}_{11} - \bar{u}_{22}$  and  $\bar{u}_{12}$  can be estimated as  $\Delta k/G$ , one obtains for them an estimate of  $\sim 10^{-4}$ , which exactly fits with our above estimates, and gives the same magnitude for  $\epsilon_{xx} - \epsilon_{yy} \sim 10^{-5}$ .

The model of the mixture of phases also contradicts the principles of the theory of macroscopic inhomogeneous structure formation near phase transitions [23], since the formation of such domains (nucleation) is associated with a positive contribution to the elastic energy, which is proportional not to the domain’s surface, but to the volume, and therefore is extremely large. In other words, nucleation of a new phase inside the volume of a body (not on the surface) can take place only in liquid, and never in crystal, which has a non-zero elastic shear modulus. The appearance and existence of such nucleation under conditions close to those of equilibrium (as in the experiments with quartz) is not thermodynamically consistent and cannot be accepted.

## References

- [1] van Tendeloo G, van Landuyt J and Amelinckx S 1976 *Phys. Status Solidi a* **33** 723
- [2] Soula V, Abe K, Bastie P, Dolino G, Capelle B and Zeng Y L 1993 *Phys. Rev. B* **48** 6871
- [3] van Landuyt J, Van Tendeloo G and Amelinckx S 1986 *Phys. Rev. B* **34** 2004
- [4] Yamamoto N, Tsuda K and Yagi K 1988 *J. Phys. Soc. Japan* **57** 1352
- [5] Yakovlev I A, Mikheeva L F and Velichkina T S 1956 *Dokl. Akad. Nauk SSSR* **106** 675
- [6] Shapiro S M and Cummins H Z 1968 *Phys. Rev. Lett.* **19** 361
- [7] Dolino G and Bachheimer J P 1977 *Phys. Status Solidi a* **41** 673
- [8] Dolino G 1980 *Phys. Status Solidi* **60** 391
- [9] Shustin O A, Chervich T G, Ivanov S A and Yakovlev I A 1981 *Solid State Commun.* **37** 65
- [10] Yakovlev I A and Shustin O A 1983 *Light Scattering Near Phase Transitions (Modern Problems in Condensed Matter Sciences 5)* ed H Z Cummins and A P Levanyuk (Amsterdam: North-Holland)
- [11] Dolino G 1986 *Incommensurate Phases in Dielectrics (Modern Problems in Condensed Matter Sciences 14.2)* ed R Blinc and A P Levanyuk (Amsterdam: North-Holland)
- [12] Saint-Gregoire P, Snoeck E, Rocau C, Luckyanchuk I and Janovec V 1996 *JETP Lett.* **64** 410
- [13] Berge B, Dolino G, Vallade M, Boister M and Vacher R 1984 *J. Physique* **45** 715  
Tanaka E, Ishibashi S, Abe K, Suzuki M and Shigenari T 1995 *J. Phys. Soc. Japan* **64** 136
- [14] Aslanyan T A, Shigenari T, Abe K and Ukigaya N 1997 *Proc. 9th Int. Mtg on Ferroelectricity; J. Korean Phys. Soc.* **32** 914
- [15] Aslanyan T A, Levanyuk A P, Vallade M and Lajzerowicz J 1983 *J. Phys. C: Solid State Phys.* **16** 6705
- [16] Mikheeva L F and Shustin O A 1964 *Kristallografiya* **9** 423
- [17] Shustin O A 1964 *Kristallografiya* **9** 925
- [18] Bachheimer J P 1986 *J. Phys. C: Solid State Phys.* **19** 5509
- [19] Aslanyan T A, Shigenari T and Abe K 1998 *J. Phys.: Condens. Matter* **8** 4565
- [20] Overhauser A W 1971 *Phys. Rev. B* **3** 3173
- [21] Axe J D 1980 *Phys. Rev. B* **21** 4181
- [22] Aslanyan T A, Shigenari T and Abe K 1997 *Proc. 9th Int. Mtg on Ferroelectricity; J. Korean Phys. Soc.* **32** 910
- [23] Roitburd A L 1974 *Usp. Fiz. Nauk* **113** 69
- [24] Gouhara K and Kato N 1983 *J. Phys. Soc. Japan* **52** 3821
- [25] Bastie P and Dolino G 1985 *Phys. Rev. B* **31** 2857