# A novel type of incommensurate phase in quartz: The elongated-triangle phase

P. Saint-Grégoire, E. Snoeck and C. Roucau
*CEMES-LOE, BP 4347, 31055, Toulouse, Cédex, France*

I. Luk'yanchuk
*L. D. Landau Institute for Theoretical Physics, Moscow, Russia*

V. Janovec
*University of Technology, 16117, Liberec, Czech Republic; Institute of Physics, Academy of Sciences of the Czech Republic, 18040 Prague, Czech Republic*

(Submitted 25 July 1996; resubmitted 20 August 1996)
Pis'ma Zh. Éksp. Teor. Fiz. **64**, No. 5, 376–381 (10 September 1996)

We present evidence for a thermodynamically stable incommensurate elongated-triangle (ELT) phase in quartz, observed by transmission electron microscopy at the $\alpha$–$\beta$ structural transition. The phase sequence on cooling is: incommensurate equilateral-triangle (EQT) phase (ferroelectric)—incommensurate ELT (ferroelectric and ferroelastic)—uniform $\alpha$ phase. The ELT blocks could be responsible for the large light scattering in the vicinity of the $\alpha$–$\beta$ transition. © *1996 American Institute of Physics.* [S0021-3640(96)01517-4]

PACS numbers: 61.16.Bg, 64.70.Rh.

Although the $\alpha$–$\beta$ structural phase transition in quartz has been known for more then a century, interest has been renewed in the last decades due to the discovery of an incommensurate phase existing between the $\alpha$ (low-temperature) and $\beta$ (high-temperature) phases, in a temperature range of approximately 1 K around 847 K (see Refs. 1 and 2 for a review). The $\beta$ phase is hexagonal with space group $P6_z2_x2_y$, having $x$- and $y$-type basal-plane twofold axes. The $\alpha$–$\beta$ transition is induced by a rotation of the $SiO_4$ tetrahedra about the $x$ axes by an angle $\eta$ (Ref. 3), which reduces the symmetry of the $\alpha$ phase to $P3_z2_x$. The main mechanism of the incommensurate structure formation was shown by Aslanyan *et al.*[4] to be the strong coupling between the elastic strain and the spatial gradient of $\eta$ which is responsible for a finite-$q$ instability of $\eta$ at the critical temperature $T_i$ and for a regular spatially modulated structure of $\eta(r)$ between $T_i$ and the lock-in transition temperature, below which the system recovers homogeneity of $\eta$.

Transmission electron microscopy (TEM) displays the incommensurate state as a regular triangular pattern of equilateral microdomains with $\pm\eta$ (Refs. 5–7). This equilateral-triangle (EQT) phase corresponds to the minimum of the Landau functional calculated in Ref. 4. Close to lock-in this structure is often perturbed by elongated dagger-shaped triangles pointing in several directions, so that the global organization looks rather chaotic. From this, one could suspect[6] that a new phase attempts to nucleate in the vicinity of the lock-in transition, but a large thermal gradient is perturbing its formation.

  

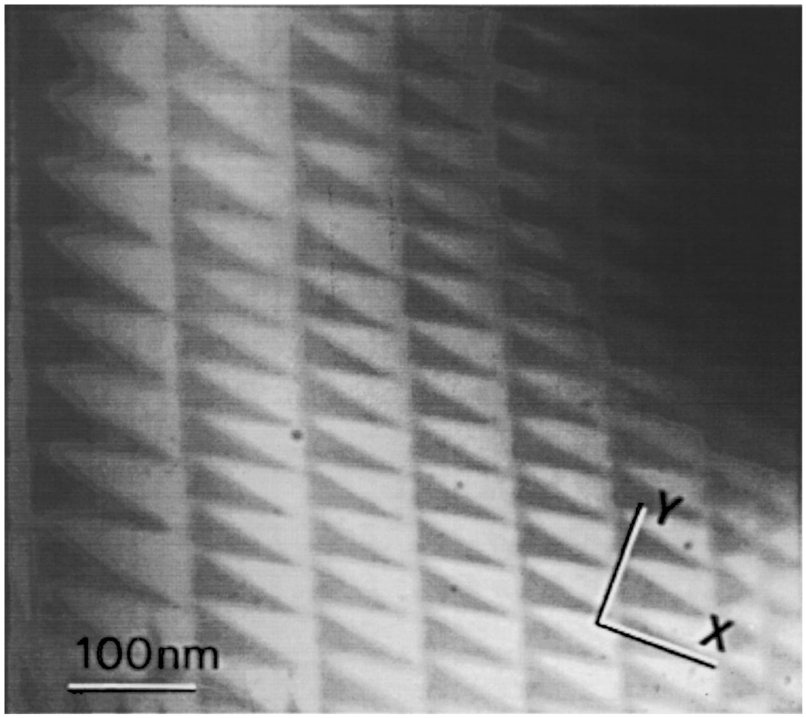


FIG. 1. Dark field image (TEM, Bragg spot (110)) of the ELT phase.

In this letter we report the first TEM observation of the new incommensurate elongated-triangle (ELT) phase which is formed in a small temperature region near the lock-in transition. From the free energy calculations we claim that near the lock-in transition the ELT phase becomes thermodynamically more stable than the EQT phase, and ideally the sequence of phases EQT–ELT–$\alpha$ should appear as the temperature decreases. Finally, we relate the ELT blocks with optical inhomogeneities that could be responsible for the huge light scattering at the $\alpha$–$\beta$ transition.

In our TEM experiments, as in Ref. 8, the specimens were first mechanically polished until a thickness of approximately 300 $\mu$m was reached, then further polished with the help of a dimpling device until the central area reached 20 $\mu$m; finally, an ionic thinning (argon, at a 15° angle of incidence) produced samples sufficiently transparent to electrons. To minimize damage due to the electron bream, the observations started at temperatures close to the $\alpha$–$\beta$ transition. Experiments were performed with a JEOL 200 CX electron microscope.

Under these conditions the ELT phase was observed just above the $\alpha$ phase in a narrow temperature interval of about 0.1 K, estimated from its spatial extent in the presence of a temperature gradient. We obtained micrographs showing regular ELT texture over regions of about 1000 nm (Fig. 1). In this temperature interval the distance between consecutive parallel walls is of the order of 100 nm. The orientation of elongated

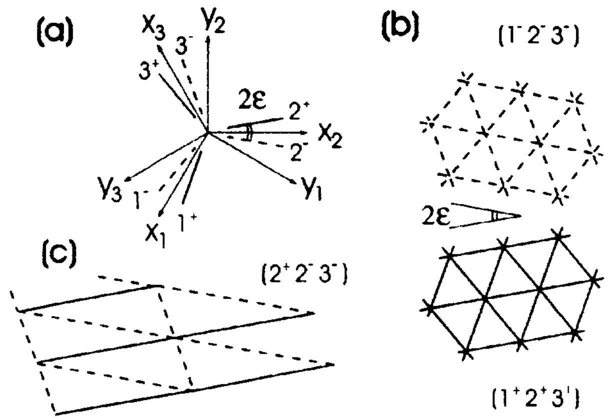


FIG. 2. Domain walls (a) EQT (b), and ELT (c) textures in quartz.

triangles in different experiments was not correlated with the direction of the temperature gradient. We also observed the nucleation of the ELT phase from the bulk EQT phase. All of this indicates an intrinsic stability of the ELT phase. The EQT-to-ELT phase transition is of the first order, and both phases may coexist in the crystal.

We now show that the observed ELT phase does become energetically more stable than the EQT phase near the lock-in transition. We follow the domain-wall approach,[9] treating the incommensurate state as a texture of interacting domain walls with junctions and intersections between them. This approximation seems to be relevant near the lock-in transition, where the domain-like spatial distribution of $\eta(r)$ is indeed observed by TEM, the width $\xi$ of the domain walls being substantially smaller than the distance $h$ between them. The calculations we present here are of the same nature as those in the study of the commensurate–incommensurate transition in $2H$-$TaSe_2$ and in inert gas layers adsorbed on graphite.[10]

Three contributions to the energy of a domain texture are: (i) The energy of the domain walls. (ii) The interaction between nonparallel walls which cross at the vertices; we add to this contribution the energy of the vertices themselves and call all together the "vertex energy." (iii) The interaction between parallel domain walls.

(i) The energy of isolated domain walls is a function of their orientation and temperature. According to TEM observations the domain walls in quartz are parallel to the $z$ axis and only approximately parallel to the $x$-type crystallographic axes. Walker concluded[9] that the walls are tilted away from the $x$-type axes by a small angle $\varepsilon$, which is 10°–15° near lock-in and which vanishes near $T_i$, according to Landau functional calculations.[4] The reason for this is that the exact $x$ orientation is not symmetry-preferred because the point symmetry group $2_z'$ (the prime is a reminder that the operation changes the sign of $\eta$) of a domain wall slightly rotated around $z$ is the same as for the wall of $x$-orientation.[11]

Figure 2a shows six equivalent equilibrium orientations of domain walls with tilt angles of $\pm\varepsilon$ for $1^{\pm}$, $2^{\pm}$, $3^{\pm}$ walls participating in domain texture formation. The EQT

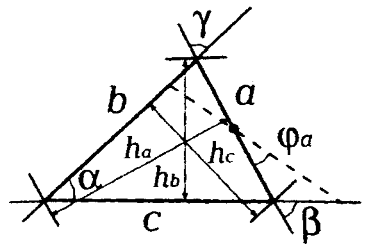


FIG. 3. Parametrization of the triangular domain texture.

structure is formed by the equidistant sets of either $1^+$, $2^+$, $3^+$ or $1^-$, $2^-$, $3^-$ domain walls, as shown in Fig. 2b. These two degenerate states form blocks of the EQT phase (with a typical size of 0.6–1 $\mu$m) which are rotated by $\pm\varepsilon$ with respect to the crystallographic $x$-type axes. We identify the ELT phase with a triangular structure having internal angles $2\varepsilon$, $120°-2\varepsilon$, 60°. Six block states are possible. The ELT phase corresponding to the set ( $2^+$,$2^-$,$3^-$) is sketched in Fig. 2c.

To account for the lock-in transition we assume that the domain-wall energy is positive in the $\alpha$ phase and changes sign at $T=T_0$ in the incommensurate state, where the free energy is lowered by a packing of a large number of walls into a lattice which is stabilized by the repulsion between walls and the positive vertex energy.[6] The energy per unit length of a wall slightly tilted from its equilibrium orientation by a small angle $\varphi$ is:

$$e=A(T_0-T)+G\varphi^2 \tag{1}$$

with $G>0$. The increase of the distances between domain walls near the lock-in transition, clearly seen in TEM observations, is a consequence of the vanishing of the wall energy at $T_0$.

Domain walls with $2_z'$ symmetry carry a ferroelectric polarization along the $z$ axis which is opposite for the sets $1^+$, $2^+$, $3^+$ and $1^-$, $2^-$, $3^-$ and exhibit a nonzero elastic strain.[12]

(ii) The vertex energy $Q$ depends on the number of crossing domain walls and their orientation.

(iii) We write the interaction energy between two adjacent parallel domain walls per unit length as $Be^{-h/\xi}$, where the distance $h$ between them is assumed to be larger than their width $\xi$.

To compare the energies of ELT and EQT phases quantitatively we parametrize their geometrical structure as shown in Fig. 3. We also examine the stability of these phases with respect to a slight tilting of the edges $a$, $b$, $c$ from their equilibrium orientations e.g. $2^+$, $2^-$, $3^-$ for the ELT phase and $1^+$, $2^+$, $3^+$ for the EQT phase) by angles $\varphi_a$, $\varphi_b$, $\varphi_c$. Then the vertex angles $\alpha$, $\beta$, $\gamma$ of the triangles are written as $\alpha=\alpha_0-\varphi_c+\varphi_b$, $\beta=\beta_0-\varphi_a+\varphi_c$, and $\gamma=\gamma_0-\varphi_b+\varphi_a$, where $\alpha_0$, $\beta_0$, $\gamma_0$ are the angles for the equilibrium orientation, which are 60° for the EQT phase and $2\varepsilon$, $120°-2\varepsilon$, 60°, respectively, for the ELT phase.

The energy of the domain texture per unit area is expressed as

$$\mathscr{F}=\frac{1}{S}\left[\frac{1}{2}(e_a a+e_b b+e_c c)+\frac{1}{2}Q+B(ae^{-h_a/\xi}+be^{-h_b/\xi}+ce^{-h_c/\xi})\right], \tag{2}$$

where $Q$ (either $Q_{\mathrm{ELT}}$ or $Q_{\mathrm{EQT}}$) is the vertex energy. The domain-wall energy $e_w(w=a,\ b,\ c)$ is given by (1) with $\varphi=\varphi_w$. Close to $T_0$ the third term in (2) becomes small in comparison with the second one. The most stable configuration is the result of minimization of (2). We choose $S$ and $\varphi_a,\ \varphi_b,\ \varphi_c$ as variational parameters, taking into account the relations $a=\sqrt{2S}\nu_a,\ h_a=\sqrt{2S}/\nu_a$, where $\nu_a=(\sin\alpha/\sin\beta\sin\gamma)^{1/2}$, and the analogous expressions for $b,\ h_b,\ \nu_b$ and $c,\ h_c,\ \nu_c$. Neglecting the interaction of parallel walls, minimizing $\mathscr{F}$ with respect to $S$, and expanding the result in the small parameters $\varphi_a,\ \varphi_b,\ \varphi_c$, we obtain:

$$\mathscr{F}=-[A(T_0-T)\cdot p+A(T_0-T)(\zeta_a\varphi_a+\zeta_b\varphi_b+\zeta_c\varphi_c)+G(\varphi_a^2+\varphi_b^2+\varphi_c^2)p]^2\frac{1}{2Q}, \tag{3}$$

where $p=\nu_a+\nu_b+\nu_c$, $\zeta_a=\frac{1}{2}(\nu_c-\nu_b)(\cot\beta+\cot\gamma)+\frac{1}{2}\nu_a(\cot\beta-\cot\gamma)$ and the analogous expressions for $\zeta_b$ and $\zeta_c$ at $\alpha=\alpha_0,\ \beta=\beta_0,\ \gamma=\gamma_0$. When $T\rightarrow T_0$, $S$ diverges as $2Q^2/p^2A^2(T_0-T)^2$. Below the lock-in transition the domain texture is absent and $\mathscr{F}=0$.

For the EQT phase we have $p\simeq 3.2$ and $\zeta_a,\ \zeta_b,\ \zeta_c=0$. With $\varphi_a,\ \varphi_b,\ \varphi_c=0$ we have

$$\mathscr{F}_{\mathrm{EQT}}\simeq -5.2A^2(T_0-T)^2/Q_{\mathrm{EQT}}. \tag{4}$$

For the ELT phase with $\varepsilon=10^\circ$ one obtains $p\simeq 4.9$, $\zeta_a\simeq -0.28$, $\zeta_b\simeq -3.6$, $\zeta_c\simeq 3.9$. Minimization of (3) with respect to $\varphi_a,\ \varphi_b,\ \varphi_c$ yields:

$$\mathscr{F}_{\mathrm{ELT}}\simeq -8.2A^2(T_0-T)^2/Q_{\mathrm{ELT}}. \tag{5}$$

We find that $\mathscr{F}_{\mathrm{ELT}}<\mathscr{F}_{\mathrm{EQT}}$ if $Q_{\mathrm{EQT}}/Q_{\mathrm{ELT}}>0.6$, and the ELT phase appears to be more stable then the EQT phase.

The above conclusion is valid only close to the lock-in transition, where the interaction between parallel walls is negligible because of the large distance $h$ between them. The interaction of adjacent walls becomes important at higher temperatures, where $h$ is smaller. Assuming now that in this temperature region the third term in (2) is dominant, we find that the EQT phase, as the state with the maximal wall concentration is the most stable. This is compatible with Landau functional calculations[4] which show that the EQT phase is stable near $T_i$. This qualitative consideration shows that at some critical temperature $T^*$, $T_0<T^*<T_i$, the first-order phase transition between the ELT and EQT phases is expected.

Since the EQT phase is formed by walls carrying an electric polarization along $z$, it exhibits macroscopic *ferroelectricity* with the opposite direction of $P_z$ for blocks $1^+,2^+,3^+$ and $1^-,2^-,3^-$, which can be identified with ferroelectric domains. The nonzero elastic strains of the walls cancels out on average for the EQT phase. These properties[12] follow from the $6_z'$ point symmetry of the EQT phase.[14] In contrast, the $2_z'$ point symmetry of the ELT phase is compatible with both the $z$-directed ferroelectricity and the basal-plane spontaneous strain of the crystal. The ELT phase is formed by the $+$ and $-$ domain walls (carrying opposite polarizations along $z$) which have a different density, so the macroscopic polarization as well as the resulting elastic strain does not vanish, and the blocks can be identified with ferroelastic and ferroelectric domains. We note that the ELT phase in quartz is the first example of an incommensurate state which is both *ferroelastic* and *ferroelectric*.

The appearance of the ELT phase sheds light on the old problem of the anomalously strong small-angle light scattering at the $\alpha$–$\beta$ transition in quartz,[16] which is caused by static columnar optical inhomogeneities with a cross section of $\sim$20 $\mu$m which appear in a small temperature interval of $\sim$0.1 K in the region of the $\alpha$–$\beta$ transition. These inhomogeneities cannot be associated with $\pm P_z$ EQT blocks, which possess the same optical indicatrix because of their $6_z'$ symmetry. In contrast, the ELT ferroelastic blocks have optical indicatrices of different orientation, which results in spatial inhomogeneity of the refractive index. We can therefore conclude that this inhomogeneity is the main source of the huge light scattering in quartz.

CEMES is UPR CNRS No. 8011, G. D. P. C. is UMR CNRS No. 233. The work of I. L. was supported by the Russian Fund for Fundamental Research (RFFR), Grant No. 960218431a. The work of V. J. was supported by Grant agency of Czech Rep. (No. 202/96/0722).

[1] G. Dolino, in *Incommensurate Phases in Dielectrics*, Vol. 2, eds. R. Blinc and A. P. Levanyuk (North Holland, Amsterdam, 1986), p. 206.
[2] G. Dolino and P. Bastie, Key Engineering Materials (TRANSTECH publ.) **101–102**, 285 (1995).
[3] H. Grimm and B. Dorner, J. Phys. Chem. Solids **36**, 407 (1975).
[4] T. A. Aslanyan *et al.*, J. Phys. C **16**, 6705 (1983).
[5] G. Van Tendeloo, J. Van Landuyt, and S. Amelinckx, Phys. Status Solidi A **30**, K11 (1975).
[6] J. Van Landuyt *et al.*, Phys. Rev. B **31**, 2986 (1985).
[7] G. Van Tendeloo, J. Van Landuyt, and S. Amelinckx, Phys. Status Solidi A **33**, 723 (1976).
[8] E. Snoeck, C. Roucau, and P. Saint-Grégoire, J. Phys. (Paris) **47**, 2041 (1986).
[9] M. B. Walker, Phys. Rev. B **28**, 6407 (1983).
[10] P. Bak *et al.*, Phys. Rev. B **19**, 1610 (1979).
[11] P. Saint-Grégoire and V. Janovec, Lecture Notes Phys. **353**, 117 (1989).
[12] M. B. Walker and R. J. Gooding, Phys. Rev. B **32**, 7408 (1985).
[13] P. Saint-Grégoire *et al.*, Ferroelectrics **125**, 209 (1992).
[14] P. Saint-Grégoire *et al.*, Phys. Status Solidi A **139**, 361 (1993).
[15] P. Saint-Grégoire, Key Engineering Materials (TRANSTECH publ.) **101–102**, 237 (1995).
[16] I. A. Yakovlev, L. F. Mikheeva, and T. S. Velichkina, Kristallografiya **1**, 123 (1956) Sov. Phys. Crystallogr. **1**, 91 (1956).
[17] For a review see: I. A. Yakovlev and O. A. Shustin, in *Light Scattering Near Phase Transitions*, eds. H. Z. Cummins and A. P. Leuk (North Holland, Amsterdam, 1983), p. 605.

Published in English in the original Russian journal. Edited by Steve Torstveit.