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A NOVEL-TYPE INCOMMENSURATE PHASE IN QUARTZ: THE ELONGATED-TRIANGLE PHASE

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We present the evidence for a thermodynamically stable incommensurate elongated-triangle (ELT) phase in quartz observed by transmission electron microscopy at structural $\alpha - \beta$ transition. The phase sequence on cooling is: incommensurate equilateral-triangle (EQT) phase (ferroelectric) - incommensurate ELT (ferroelectric and ferroelastic) - uniform α phase. The ELT blocks could be responsible for the large light scattering in the vicinity of $\alpha - \beta$ transition.

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Although the structural α-β phase transition in quartz is known since more then a century, interest has be renewed in the last decades due to discovery of an incommensurate phase existing between α (low temperature) and β (high temperature) phases, in a temperature range of approximately 1 K around 847 K (For a review see [1][2]). The β phase is hexagonal with the space group $P6_z2_x2_y$ having x and y type basal plane binary axes. The α-β transition is induced by a rotation of SiO_4 tetrahedra around x axes by an angle η [3] which reduces symmetry of the α 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 η which is responsible for a finite-q instability of η at the critical temperature T_i and for a regular space modulated structure of $\eta(r)$ between T_i and lock-in transition temperature below which the system recovers homogeneity of η.

Transmission electron microscopy (TEM) display the incommensurate state as a regular triangular pattern of equilateral microdomains with $\pm\eta$[5] [6] [7] [8]. This Equilateral-Triangle (EQT) phase corresponds to the minimum of Landau functional calculated in [4]. Close to lock-in this structure is often pertrubated 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 large thermal gradient is perturbing its formation.

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 lock-in transition. From the free energy calculations we claim that ELT phase nearby lock-in transition becomes thermodynamically more stable then EQT phase and ideally the sequence of phases EQT -ELT -α should appear when temperature decreases. Finally, we relate the ELT blocks with the optical inhomogeneities which could be responsible for the huge light scattering at the $\alpha - \beta$ transition.

In our TEM experiments, similarly as in [8], the specimens were first mechanically polished until a thickness of approximately 300 μm was reached, then further polished with the help of a dimpling device until the central area reached 20 μm; finally, an ionic thinning (argon, under a 15^0 angle of incidence) allowed one to obtain samples sufficiently transparent to electrons. To minimize damages duê to the electron beam, the observations started at temperatures close to the $\alpha - \beta$ transition. Experiments were performed with a JEOL 200 CX electron microscope.

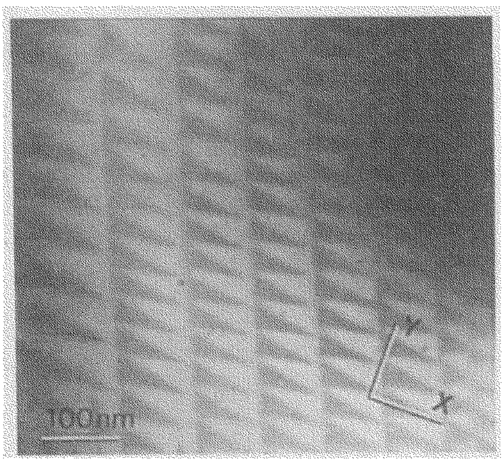

Fig.1. Dark field image (TEM, Bragg spot (110)) of ELT phase.

In these conditions the ELT phase was observed just above the α phase in a narrow temperature interval of about $0.1K$, estimated from its spatial extension in presence of a temperature gradient. We obtained the micrographs showing regular ELT texture in ranges of about 1000 nm (Fig.1). In this temperature region the distance between consecutive parallel walls is of the order of 100 nm. The orientation of elongated triangles in different experiments was not correlated with the direction of thermal gradient. We observed also the nucleation of the ELT phase from the bulk of EQT phase. All of this indicates an intrinsic stability of ELT phase. The EQT to ELT phase transition is of the first order and both phases may coexist in the crystal.

Now, we show that the observed ELT phase does become energetically more stable then EQT phase near lock-in transition. We follow the domain wall approach [9] considering the incommensurate state as a texture of interacting domain walls with junctions and intersections between them. This approximation seems to be relevant nearby lock-in transition where the domain-like space distribution of $\eta(r)$ is indeed observed by TEM, the width of domain walls ξ being substantially smaller then 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 rare-gas layers adsorbed on graphite [10].

Three contributions to the energy of a domain texture are: (i) The energy of the domain walls. (ii) Interaction between nonparallel walls which cross in the vertices; we include to this contribution the energy of the vertices themselves and call all together the "vertex energy". (iii) 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 ε, which is of 10^0-15^0 near lock-in and vanishes near T_i according to Landau functional calculations [4]. The reason for this is that the exact x orientation is not symmetrically prominent because the point symmetry group $2'_z$ (the prime reminds that the operation changes the sign of η) of a domain wall slightly rotated around z is the same as for the wall of x-orientation [11].

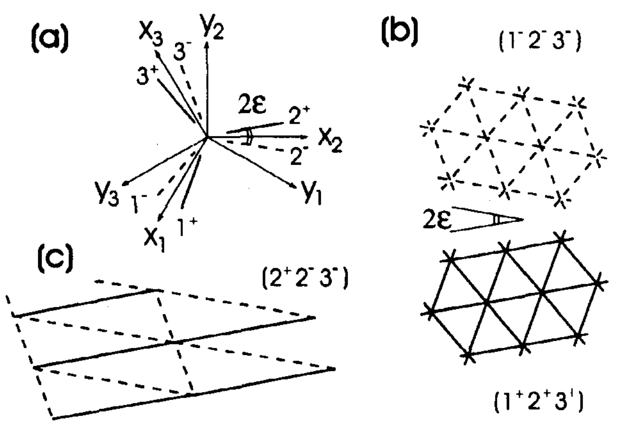

Fig.2. Domain walls (a), *EQT* (b) and *ELT* (c) textures in quartz.

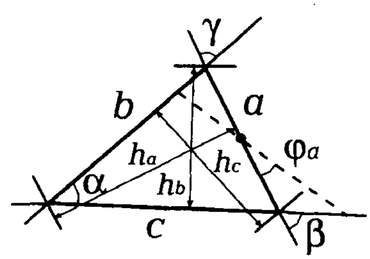

Fig.3. Parametrization of triangular domain texture.

Fig.2a shows six equivalent equilibrium orientations of domain walls with tilting angles of $\pm\varepsilon$ for $1^\pm, 2^\pm, 3^\pm$ walls participating in domain texture formation. The *EQT* 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 *EQT* phase (with typical size of $0.6-1\mu m$) which are rotated by $\pm\varepsilon$ with respect to the crystallographical x-type axes. We identify *ELT* phase with a triangular structure having internal angles 2ϵ, $120^0-2\epsilon$, 60^0. 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 walls energy is positive in the α phase and changes its 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 φ 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 the consequence of vanishing of the walls energy at T_0.

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

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

(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 then their width ξ.

To compare the energies of ELT and EQT phases quantitatively we parametrize their geometrical structure as shown in Fig.3. We examine also the stability of these phases with respect to the slight tilting of the edges a,b,c from their equilibrium orientations (e.g. $2^+, 2^-, 3^-$ for ELT phase and 1^+,2^+,3^+ for EQT phase) by angles φ_a,φ_b,φ_c. Then, the triangle angles α,β,γ are presented as: $\alpha = \alpha_0 - \varphi_c + \varphi_b$, $\beta = \beta_0 - \varphi_a + \varphi_c$, $\gamma = \gamma_0 - \varphi_b + \varphi_a$ where α_0,β_0,γ_0 are the angles for the equilibrium orientation that are 60^0 for EQT phase and respectively $2\varepsilon, 120^0 - 2\varepsilon, 60^0$ for ELT phase.

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

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

where Q (either Q_{ELT} or Q_{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 (??) becomes small in comparison with the second one. The most stable configuration is the result of minimization of (??). We choose S and φ_a,φ_b,φ_c as variational parameters, taking into account that $a = \sqrt{2S}\nu_a$, $h_a = \sqrt{2S}/\nu_a$, where $\nu_a = \left(\frac{\sin\alpha}{\sin\beta\sin\gamma}\right)^{1/2}$ and the analogous expressions for b, h_b, ν_b, c, h_c, ν_c. Neglecting the parallel walls interaction, minimizing $\mathcal{F}$ over S and expanding the result over the small values of φ_a,φ_b,φ_c we obtain:

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

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

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

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

For ELT phase with $\varepsilon = 10^0$ 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:

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

We get that $\mathcal{F}_{ELT} < \mathcal{F}_{EQT}$ if $Q_{EQT}/Q_{ELT} > 0.6$ 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 adjacent walls interaction becomes important at higher temperatures where h diminishes. Assuming now that in this temperature region the third term in (??) is dominating we obtain that the EQT phase is the most stable one as the state with the maximal wall concentration. This is compatible with Landau functional calculations [4] which gives the stability of EQT phase nearby 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 EQT phase is formed by walls carrying an electric polarization along z it exhibits the macroscopic *ferroelectricity* with the opposite direction of P_z for $1^+,2^+,3^+$ and $1^-,2^-,3^-$ blocks which can be identified with ferroelectric domains. The nonzero elastic strain of walls compensates in average for EQT phase. These properties [12] follow from the $6'_z$ point symmetry of EQT phase [14]. In contrast, the $2'_z$ point symmetry of 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 blocks can be identified with ferroelastic and ferroelectric domains. Note, that the ELT phase in quartz is the first example of incommensurate state which is both *ferroelastic* and *ferroelectric.*

The appearance of ELT phase sheds light on the old problem of the anomalous strong small-angle light scattering at $\alpha-\beta$ transition in quartz [16] which is caused by static columnar optical inhomogeneities of cross section of $\sim 20\mu m$ which appear in a small temperature interval of $\sim 0.1K$ in the region of $\alpha-\beta$ 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 the spatial inhomogeneity of the refraction index. We can conclude therefore that this inhomogeneity is the main source of the huge light scattering in quartz.

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