

# Possibility of a noncommensurate phase near the $\alpha \rightleftharpoons \beta$ transition point in quartz

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The possibility is considered of formation of a long-period incommensurate superstructure near the  $\alpha \rightleftharpoons \beta$  transition point in quartz. Account is taken of the interaction of the soft phonon branch with the acoustic branch. An essential role is played here by the decrease of the modulus of hydrostatic compression near the transition point, as established by fluctuation effects.

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Some time ago, electron-microscopy methods have revealed that quartz is in a spatially inhomogeneous state near the  $\alpha \rightleftharpoons \beta$  transition point.<sup>(1,2)</sup> This inhomogeneity has the character of a two-dimensional periodic structure with a period on the order of tenths or hundredths of a micron, and can be represented in the manner shown in Fig. 1. The latest experiments of Shustin *et al.*<sup>(3)</sup> on light scattering have also revealed a long-period inhomogeneity near the transition point (albeit with a period on the order of 20  $\mu\text{m}$ ) in a temperature interval on the order of 0.1 K. The purpose of the present paper is to discuss some possible causes of this inhomogeneity.

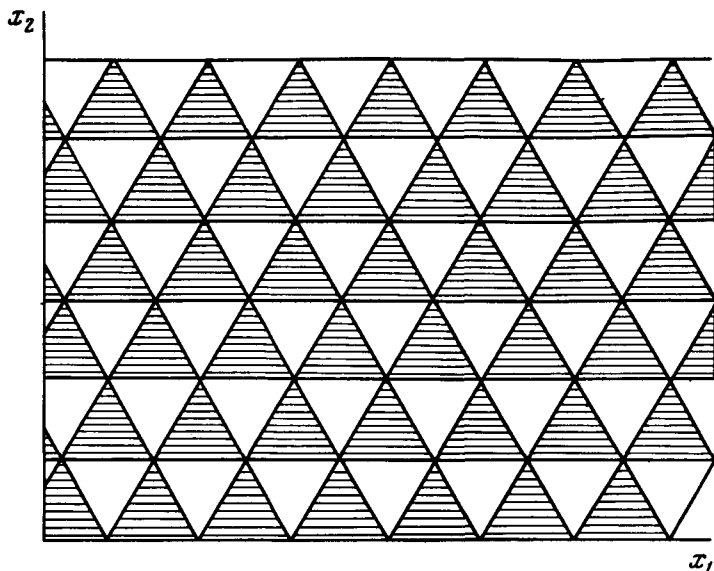


FIG. 1. Form of the distribution of the transition parameter  $\eta(R)$  in a plane perpendicular to a threefold axis near the point of the  $\alpha \rightleftharpoons \beta$  transition in quartz. The  $x_1$  is directed along a twofold axis that is preserved in a transition to the asymmetrical phase. The dark and light triangles correspond to positive and negative values of  $\eta(R)$ , respectively.

We note first that this inhomogeneity cannot constitute elastic domains, since the spontaneous deformation in the  $\alpha \rightleftharpoons \beta$  transition has one sign. We advance below the point of view that this inhomogeneity is a long-period noncommensurate superstructure. The cause of the formation of the noncommensurate structure can be, in particular, a definite interaction between vibrational modes of different symmetry,<sup>[4,5]</sup> and interaction that is reflected by the presence of definite invariants in the expansion of the thermodynamic potential.

In our case this expansion takes the form

$$\Phi = \Phi_0 + \frac{A}{2} \eta^2 + \frac{B}{4} \eta^4 + \frac{a}{2} \left[ (u_{11} - u_{22}) \frac{\partial \eta}{\partial x_1} - 2 u_{12} \frac{\partial \eta}{\partial x_2} \right] + \frac{K}{2} (u_{11} + u_{22})^2 + \frac{\mu}{2} [(u_{11} - u_{12})^2 + 4 u_{12}^2] + r \eta^2 (u_{11} + u_{22}) + c \eta^2 \left( \frac{\partial^3 \eta}{\partial x_1^3} - 3 \frac{\partial^3 \eta}{\partial x_2^2 \partial x_1} \right). \quad (1)$$

Explicit accounts are taken here of only terms that are essential in what follows. The  $x_1$  axis is directed along a two-fold axis that is preserved in the transition to the  $\alpha$  phase, the  $x_3$  axis is oriented in a sixfold order direction  $\eta$  is a parameter of the transition, the term with the coefficient  $a$  reflects the interaction of the "optical" deformation corresponding to  $\eta$  with the "acoustic" deformations  $u_{ik}$ . Let us analyze

the conditions under which the  $\beta$  phase loses stability. Eliminating the deformations from (1) and leaving out terms of order higher than the second we find:

$$\Phi = \int \widetilde{\Phi} dV = V \sum_{\mathbf{k}} \Phi_{\mathbf{k}}$$

$$\Phi_{\mathbf{k}} = \frac{1}{2} \left[ A + g k^2 - \frac{a^2 k^2}{4} \left( \frac{1}{K + 2\mu} + \frac{\sin^2 3\phi}{2\mu} \right) \right] \eta_{\mathbf{k}} \eta_{-\mathbf{k}}, \quad (2)$$

where  $\phi$  is the angle between the vector  $\mathbf{k}$  and the  $x_1$  axis. We see therefore that at

$$\frac{a^2 k^2 + 4\mu}{8\mu(K + 2\mu)} > g, \quad (3)$$

the stability coefficient is maximal at  $k=0$  and it decreases most rapidly when  $\mathbf{k}$  increases in the direction  $\phi = (\pi/6) + \pi n$ , i.e., in the directions of the twofold axes that vanish as a result of the transition from the  $\beta$  to the  $\alpha$  phase. We note that the dependence of the stability coefficient on  $\phi$  is evidence of a nonanalytic character of its dependence on the components of the wave vector  $\mathbf{k}$ , which appears as a result of the interaction of the optical and acoustic deformation. This circumstance was noted by us in<sup>[6]</sup>. It is perfectly possible that the condition (3) is not satisfied far from the phase-transition point, but is satisfied close enough to the point where the symmetrical phase loses stability relative to the inhomogeneous fluctuations of  $\eta$ : it is known that owing to the so-called fluctuation effects the elastic modulus  $K$  decreases like  $(T - T_c)^{1/2}$  in the region of small corrections to the Landau theory<sup>[7]</sup> and like  $K \sim (T - T_c)^\alpha$  in the critical region (similarity region), where the critical exponent is  $\alpha \approx 0.1$ .<sup>[8]</sup> Putting  $K=0$  at  $T=T_c$  we verify that for quartz the left-hand side of (3) is smaller than its value far from the transition point by a factor 1.25. Far from the transition point we have  $K = 6.6 \times 10^{12}$  dyn/cm<sup>2</sup>, and  $\mu$  depends little on temperature and its value is  $\mu = 4.9 \times 10^{12}$  dyn/cm<sup>2</sup> both far from and near the transition point.

Satisfaction of condition (3) at  $T=T_c$  means that the loss of stability of the symmetrical phase takes place already at  $T > T_c$ , and moreover with respect to the onset of a spatially inhomogeneous distribution  $\eta(\mathbf{R})$ , i.e., of an incommensurate superstructure. Owing to the presence of a third-order invariant, the transition to such a structure is always of first order. Estimates show that the energy connected with the presence of a third-order invariant is comparable with the energy corresponding to the remaining terms in (1) in the interval  $|T - T_c| \approx 0.1$  K, i.e., approximately in the interval of the existence of the observed inhomogeneity. The superstructure produced thereby is a superposition of three "static waves"  $\eta$ . In the plane perpendicular to the optical axis this structure looks like the one shown in Fig. 1. It follows from (2) that the superstructure vectors are directed along twofold axes that vanish as a result of the transition to the  $\alpha$  phase. This picture is analogous to that observed in<sup>[2]</sup>. We emphasize the agreement between the directions of the superstructure vectors observed in experiment and obtained in the theory.

As already noted, a larger-scale inhomogeneity was observed in a plane perpendicular to the principal optical axis.<sup>[3]</sup> Unlike the one observed in<sup>[2]</sup>, it has an irregular character. This inhomogeneity can be connected with the breakup of the incommensurate phase into domain, as was observed in<sup>[2]</sup>. The domain boundary can serve as a source of optical inhomogeneity and can be the cause of the light diffraction observed in<sup>[3]</sup>. We note that near the phase transition into the incommensurate phase the width of the domain wall can be much larger than the period of the incommensurate superstructure.

In addition, if the explanation proposed above for the results of<sup>[2]</sup> does correspond to reality, then an approach of Brillouin line to the undisplaced component should be observed, when the temperature at which the inhomogeneity appears is approached, in the spectrum of the Brillouin scattering corresponding to a wave vector lying along a twofold axis that vanishes upon transition to the  $\alpha$  phase, at a wave-vector value close to the reciprocal characteristic dimension of the inhomogeneity.

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