# Reply to "Intermediate phase between the $\alpha$ and $\beta$ phases of quartz"

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(Received 27 January 1986)

We demonstrate that it is difficult to prove or disprove that Kato and Gouhara and ourselves are studying the same phenomena, but that the available evidence suggests that we are observing the same incommensurate structure.

The two main points in the Comment by Kato and Gouhara are concerned with our model for the incommensurate intermediate phase and with the use of optical diffraction in the interpretation of electron-microscope images. Both points have apparently not been completely understood by the authors and have hence been misquoted.

The authors apparently interpret our model as a "microtwin" model consisting of alternating triangular prisms, parallel with the $c$ axis, of $\alpha_1$ and $\alpha_2$ structure, where $\alpha_1$ and $\alpha_2$ stand for Dauphiné twins of the $\alpha$ phase of quartz (or $AlPO_4$) separated by sharp interfaces. The authors overlook, hereby, an essential feature of our model which was described in Refs. 1–3. We believe that the transition from $\alpha_1$ into $\alpha_2$ across a twin boundary occurs gradually, passing through a situation which resembles $\beta$. This can be achieved by a gradual rotation of the $SiO_4$ tetrahedra about their twofold axis. Depending on the tetrahedron considered, the rotation over a small angle that transforms $\alpha_1$ into $\alpha_2$ can occur along three different axes enclosing an angle of 120°. These rotations are coupled through the spatial framework structure of quartz, oxygen atoms being common to two tetrahedra. It is impossible to rotate a single rigid tetrahedron without causing further rotations of the coupled tetrahedra about another twofold axis. With these rotations corresponds a libration mode that transforms $\alpha_1$ into $\alpha_2$, and which causes diffuse scattering. When this mode freezes, a $3q$ state results, the satellites being situated on the diffuse intensity streaks. The resulting structure, as we have described it in Refs. 1–3, can be visualized, as in Fig. 1(a), viewed along the [0001] zone; i.e., the twin boundary regions, marked here by shading, contain a structure that gradually changes $\alpha_1 \leftrightarrow \beta \leftrightarrow \alpha_2$, as shown schematically in Fig. 1(b). Moreover, we have presented direct evidence that the boundaries sometimes visibly vibrate, and therefore, this shaded region can also be considered as a time average of $\alpha_1$ and $\alpha_2$.

This model was substantiated by the following characteristic contrast features of Dauphiné twins in electron microscopy: (i) *Domain contrast* is best observed in dark-field images made with reflections which do not belong to the [0001] zone, such as [$30\bar{3}1$], which was actually used for most of our images of the domain structure. The origin of the contrast is the difference in *magnitude* of the structure factors for reflections which are simultaneously excited in $\alpha_1$ and $\alpha_2$ giving rise to a shade difference. The reflections with the largest difference in the magnitude of the structure factor produce the most pronounced contrast difference (Fig. 2). (ii) Certain reflections belonging to the [0001] zone produce fringe patterns along the *interfaces,* but, in general, no domain contrast [see (iii)]. The origin of the contrast is now the difference in *phase* of the structure factors of simultaneously excited reflections in $\alpha_1$ and $\alpha_2$ (Fig. 3). (iii) Under multiple-beam conditions where Friedel's law is violated, weak domain contrast might result also in the [0001] zone (Fig. 4).

The presence of Dauphiné twins is also suggested by general considerations of a group-theoretical nature. The point group of $\alpha$-quartz is 32 (order 6), that of $\beta$-quartz is 622 (order 12). The symmetry element lost during the $\beta \rightarrow \alpha$ transition is a twofold axis oriented along the remaining threefold axis. The 180° rotation around this twofold axis relates the $\alpha_1$ and $\alpha_2$ variants which are Dauphiné twins.

The observation by Kato and Gouhara in x-ray diffraction of satellites also for reflections belonging to the [0001] zone is consistent with the differences in *phase* of certain

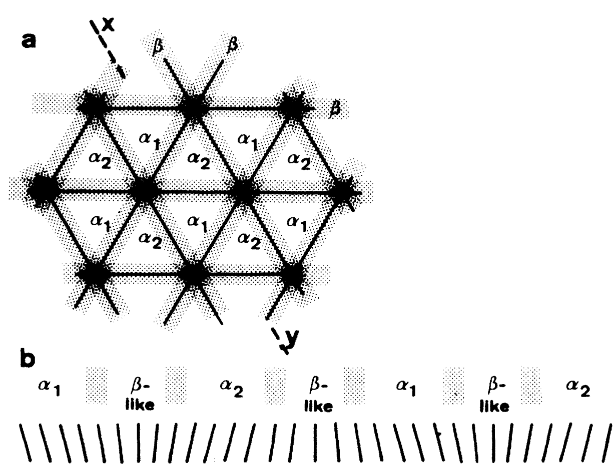


FIG. 1. Schematic representation of our model of the incommensurate modulated structure in quartz near the phase transition to the high-temperature $\beta$ phase. (a) View along the $c$ direction. $\alpha_1$ and $\alpha_2$ are the Dauphiné twin related columnar prism-shaped domains. The shaded area indicates the $\beta$-like average phase. (b) Sections through the microdomains along the plane $XY$. The line segments represent symbolically the tilt angle of the tetrahedra.

 

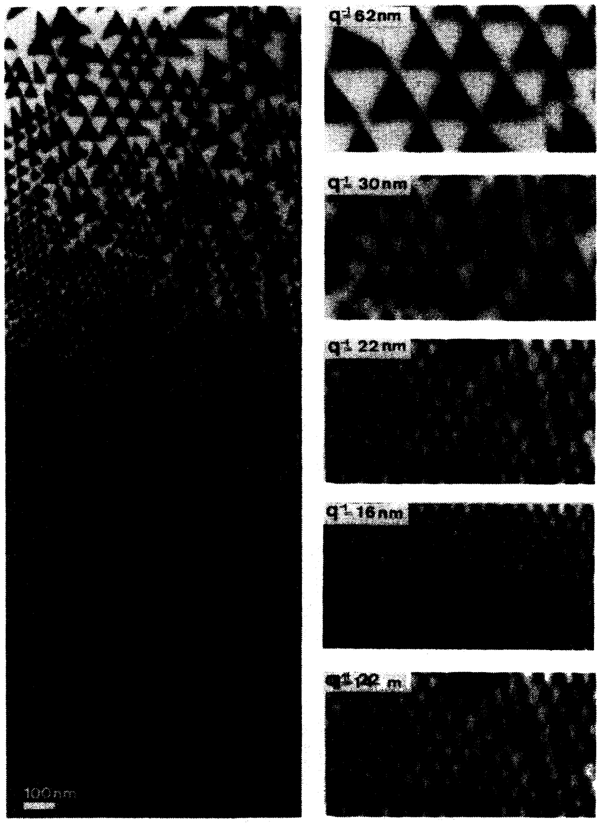


FIG. 2. Dark-field images in the (30$\bar{3}$1) reflection of the transition region from $\alpha$ to the incommensurate phase in a specimen cut perpendicular to the $c$ axis. The Dauphiné twins exhibit pronounced domain contrast due to the difference in the modulus of the structure factor for $\alpha_1$ and $\alpha_2$. Note the continuous transition from a clearly resolved lattice of triangular domains into a pattern of intersecting sinusoidal fringes. The corresponding $q$ vectors increase from 0.071 to 0.016 nm$^{-1}$.

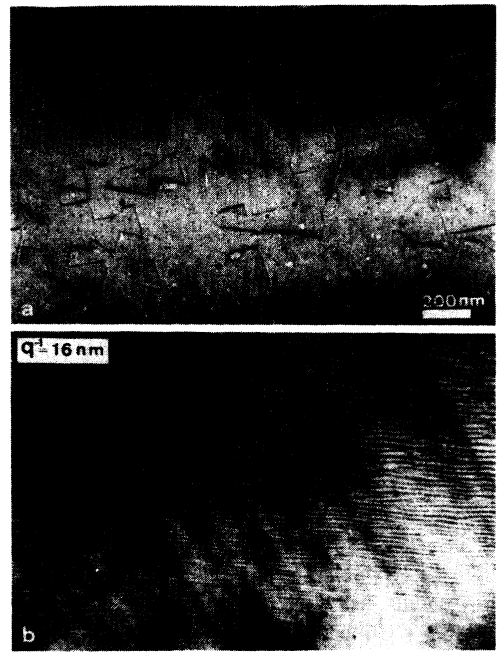


FIG. 3. Dark-field image under approximate two-beam condition in the reflection [40$\bar{4}$0] of the $c$ zone. (a) The specimen is in the $\alpha$ phase; there is no domain contrast, but the interfaces are imaged as bright or dark lines. (b) The incommensurate phase as imaged under the same conditions as (a).

structure factors for $\alpha_1$ and $\alpha_2$, which is also reflected in the contrast of Fig. 3. Moreover, the presence of $\beta$-like material along the network of interfaces, as shown in Fig. 1, contributes to the formation of a superspacing giving rise to one or several satellites.

As the temperature increases, the domain mesh size decreases (Fig. 2) and the relative width of the $\beta$-like regions, as compared to the $\alpha$ regions, becomes more important, giving rise to a more continuously varying tilt angle of the tetrahedra. Rather than interface modulated, the structure has now to be considered as deformation or displacement modulated. The resulting structure could then, perhaps, also be described as a $3q$ "configuration wave" preferred by Kato and Gouhara; this is a matter of terminology. In the absence of a detailed model for the configuration waves proposed by Kato and Gouhara, we cannot make any further comparison with our model.

According to our model, it is not surprising to find that Kato and Gouhara write "...Our recent careful examination could hardly distinguish between the intensities of the IP and $\beta$ phase at $T_Q+1$ K for nearly 100 Laue spots...."

It should be remembered that the domain size observed in electron microscopy is consistent with the magnitude of the $q$ vectors observed in x-ray and neutron diffraction, including its temperature dependence. Also, the presence of two $3q$ states, $+\phi$ and $-\phi$, differing slightly in orientation as observed in the images, is consistent with the x-ray results.[3] Our neutron-diffraction results failed to reveal these two states, due to the measuring technique used.

The main arguments of Kato and Gouhara against a "microtwin" model are based on the relative intensities of satellite reflections. According to the kinematical theory of diffraction, the intensities of satellite reflections are very sensitively dependent on the constancy of the superspacing.[4] The images suggest that this constancy is not realized, except perhaps for the smallest spacings. It is therefore not surprising to find that in Gouhara and Kato's

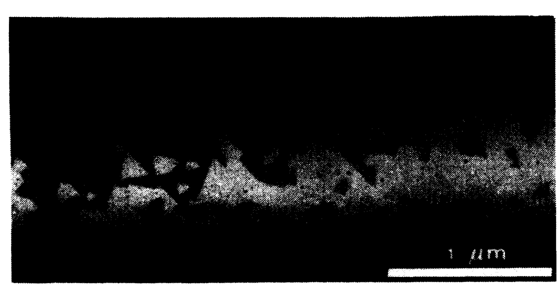


FIG. 4. Dark-field image in the reflection [20$\bar{2}$0] of the $c$ zone in a multiple-beam situation. The relatively weak domain contrast is due to the violation of Friedel's law.

x-ray results only first-order satellites are observed in most cases, and that in any case the second-order satellite, when present, has a much smaller intensity. We realize, of course, that the specimens used in x-ray diffraction may have been more perfect over larger areas than our specimens, but variations in spacing are almost inevitable.

As the mesh size decreases with rising temperature (Fig. 2), the regularity of the spacing improves and the images acquire more the aspect of sets of intersecting fringes with sinusoidal intensity variations. The transition from well-defined "triangular" domains to sets of intersecting fringes with spacings in the range from 15 to 20 nm is quite continuous, as is also the variation of the magnitude of the $q$ vector with temperature, suggesting strongly that both features are aspects of the same phenomenon.

As to the second point, we are afraid that Kato and Gouhara failed to appreciate the objective of our optical-diffraction experiments. They write "...The optical transforms of electron micrographs may not be substituted for the real satellite reflections either in electron or x-ray diffraction. . . ."

Optical-diffraction patterns of electron micrographs, especially of high-resolution images, are widely used for the analysis of image content. They are, in our view, a great help in detecting features which might be more difficult to observe directly on the image. In the present case, the optical-diffraction pattern revealed that the domain texture is sufficiently regular to produce a diffraction pattern, but not regular enough to produce a sequence of several satellites. Moreover, the experiments demonstrated clearly the spot splitting due to the presence of $+\phi$ and $-\phi$ macrodomains, which can, of course, also be observed directly on the images.[3] In particular, optical diffraction provides statistical information on small areas, which although present in the micrographs is not readily perceived. The optical-diffraction pattern of a single macrodomain also sometimes exhibits asymmetry, i.e., deviations from the hexagonal symmetry, as was also noted in the x-ray diffraction results discussed by Kato and Gouhara.[5] This can be attributed to differences in the regularity of the spacing along different $q$ directions as shown on the images.

Since we are well aware of the limitations of optical diffraction patterns of micrographs, we have not drawn more conclusions from these than could have been obtained from the images directly.

In conclusion, it seems difficult either *to prove* or *disprove* that Kato and Gouhara and ourselves are studying the same phenomena, since this would imply the use of the same specimens applying three different techniques: neutron diffraction, x-ray diffraction, and electron microscopy, which is clearly impossible because totally different specimen sizes are required. Nevertheless, the similarity of the observed features, especially their scale, geometry, and temperature behavior strongly suggest, in our view, that we are observing the same incommensurately modulated structure.

From the direct space evidence in transmission electron microscopy, we have been able to propose a detailed model which is consistent with all of our observations, and which is also consistent with the neutron-diffraction and x-ray diffraction results and with the relations between the satellite positions and intensities found by Kato and Gouhara. This does not preclude the possibility that the latter authors may propose a different model which satisfies also the boundary conditions.

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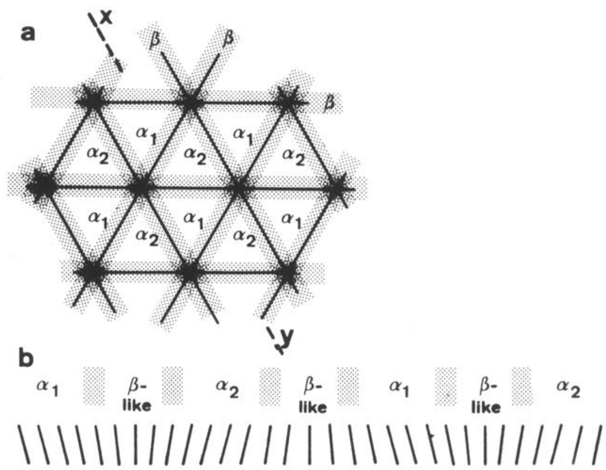


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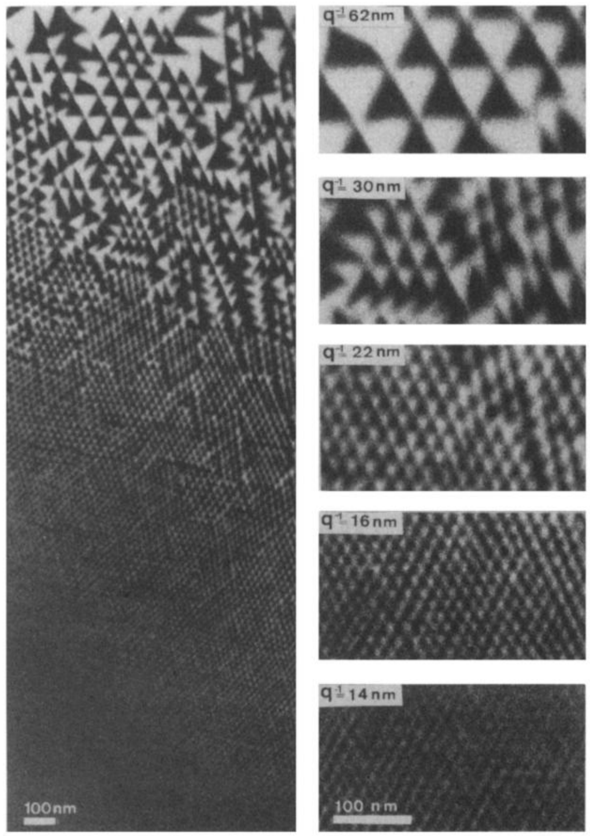


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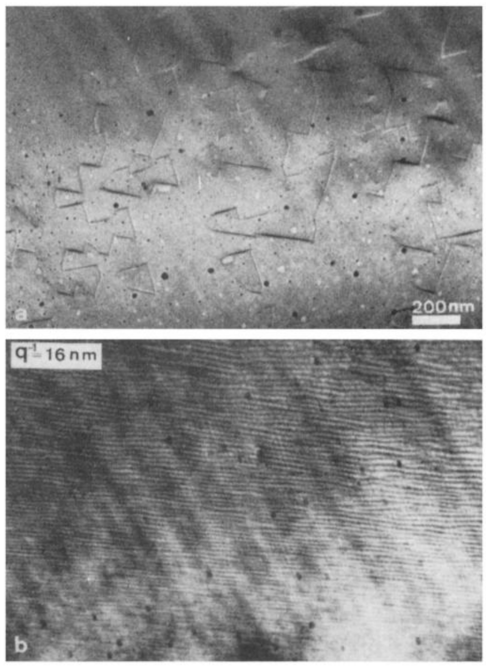


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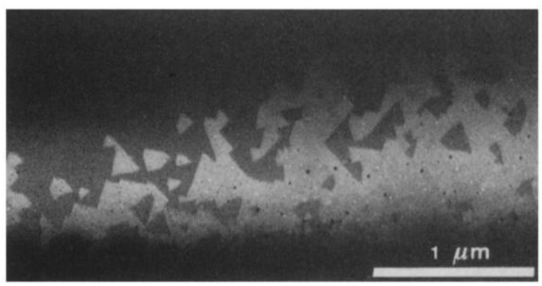


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