Intermediate phase between the α and β phases of quartz

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(Received 14 June 1985)

It is argued that the "microtwins model" for the intermediate phase of quartz, which has been proposed on the basis of electron microscope observations [for example, Phys. Rev. B **31**, 2986 (1985)], does not fit our x-ray observations, particularly the satellite reflections which depend on **g** (reflection) and **q** (modulation) vectors. The behavior in more than 20 Laue spots is well explained by the 3**q** model of "the configuration waves" which are primarily transverse.

Recently, a paper appeared on the α-β phase transition in quartz and aluminum phosphate.[1] Another similar paper[2] had appeared previously, three of the co-authors being the same as those of Ref. 1. The essence of these papers lies in their interpretation of somewhat regular arrays of triangular contrast in electron micrographs taken at a high temperature. The physical model proposed is a mixture of microtwin components α_1 and α_2, which henceforth will be referred to as the "microtwins model." Phenomenological theories[3,4] of the Landau type are used as the theoretical base of their interpretation.

One of their main conclusions seems to be that the intermediate phase (IP) which we are interested in can be interpreted by the microtwins model. In fact, the temperature dependence of the modulation vectors of the IP observed by x-ray diffraction[5] is referred to as support for their interpretation. If, however, all of our x-ray observations[6,7] and some neutron diffraction data[8] are taken into account, it is rather hard to accept the microtwins model in a literal sense for the whole of the thermodynamically stable intermediate phase which we found by x-ray topography.

This paper describes our view of the IP based on our own experimental results. More detailed arguments will be seen in forthcoming papers.[9,10] To begin, the historical development of the microtwins model and a brief summary of our x-ray observations are described in Secs. I and II, respectively.

I. MICROTWINS MODEL

To our knowledge, this model was first presented by Young[11] to interpret the temperature dependence of the x-ray structure factors of the α phase. Later, Van Tendeloo, Van Landuyt, and Amelinckx[12,13] obtained electron micrographs which are similar to those in their subsequent papers, Refs. 1 and 2. Because the contrast was similar to that of a Dauphiné twin at a low temperature, they concluded that their observation was evidence of Young's microtwins near the transiton temperature T_C. A different interpretation was given by Aslanyan and Levanyuk.[14] They suggested that the triangular structure might be a direct observation of an incommensurate phase which is expected from the Landau theory.

Following these works, Bachheimer[15] and Dolino, Bachheimer, and Zeyen[16] presented measurements of the thermal expansion, elastic compliance and birefringence,[15] and the heat capacity,[16] and they suggested the existence of an IP. Clear-cut evidence of the thermodynamically stable phase was obtained by x-ray topography[6] and heat-capacity measurements.[17] The incommensurate nature was elucidated by x-ray[5,7] and neutron diffraction.[8,16]

Here, a contravening situation arises as to whether the IP is really a mixture of Dauphiné twins or something else. It seems that adoption of the former model prevails in Europe, as manifested by Refs. 1 and 2. We believe, however, that the model does not fit our x-ray observations.

II. SUMMARY OF X-RAY OBSERVATIONS

The methods consist of *in situ* topography using the Bragg and satellite reflections and fine-beam Laue photography. Thus, information in both real and Fourier space were collected under the same sample conditions.

As to thermal conditions, two types of experiments were carried out. In one type, a slight temperature gradient was purposely applied to the specimen. The experiment was useful for obtaining an overall view of the transition. In the other, the specimen plate of 7 mm size was kept under a homogeneous temperature (± 0.1 K or less). This is necessary for obtaining quantitative information because the coexistence of different phases (especially α and IP) causes strain in the specimen. The temperature range studied and the notation of the transition points are shown in Fig. 1. Because of a large hysteresis in T_C, most experiments were carried out in the cooling run.

The α-β transition is characterized by the various structures on different levels of spatial scale.

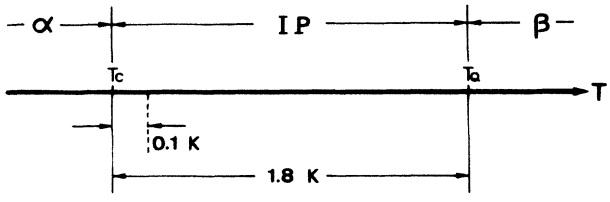

FIG. 1. The temperature range of interest.

A. A few Å (unit cell) scale

The averaged structure of the IP, which is obtainable from the intensities of the Laue spots, is sixfold-symmetric as the β phase. Our recent careful examination could hardly distinguish between the intensities of the IP and β phases at T_Q+1 K for nearly 100 Laue spots.

B. 150–300 Å scale

An incommensurate (temperature-dependent) modulated structure is excited. The modulation vectors $\pm\mathbf{q}_i$ ($i=1,2,3$) are nearly parallel to $\mathbf{b}_i$, but rotated around the **c** axis either positively or negatively. For this reason an additional specification ($\pm\phi$) is required for clarity.

C. 30–100 μm scale

The contrast of a super modulation of this scale appears in the very vicinity of T_C (with $\sim$0.1 K). The anomalous light scattering[18–20] observed prior to the establishment of the IP probably corresponds to this super modulation. A rodlike entity along the **c** axis causes an inhomogeneous strain. It is speculated that the physical origin is a commensurate phase in the matrix of the incommensurate phase.[10]

D. A few mm scale

As is well known, the Dauphiné twin exists in the α phase. In the IP, a new domain structure characterized by a $\pm\phi$ rotation of a set of $\pm\mathbf{q}_i$ vectors exists. The boundary surface includes the **c** axis. Even when the super modulation (Sec. C) appears, this domain structure is not destroyed down to T_C. So far, no direct connection between the Dauphiné twin and the new domain structure has been detected.

III. THE MODULATED STRUCTURE OF THE IP

Now we take up the principal theme of this paper. According to kinematical diffraction theory, the microtwins model predicts the following properties for the satellite reflections.

$$\text{(a)}\quad I_s(2\mathbf{q})/I_s(\mathbf{q})=\tfrac{1}{4}\ , \tag{1}$$

$$\text{(b)}\quad I_s(\pm\mathbf{q}_1)=I_s(\pm\mathbf{q}_2)=I_s(\pm\mathbf{q}_3)\ , \tag{2}$$

$$\text{(c)}\quad I_s(\mathbf{q})=0,\ \text{when } F_1=F_2\ , \tag{3}$$

where $I_s(\mathbf{q})$ denotes the intensity of a satellite reflection specified by **q**, and F_1 and F_2 are the structure factors of the α_1 and α_2 components for a given reflection vector **g**.

The relevant experimental results, on the contrary, are summarized as follows.

(a) $I_s(2\mathbf{q})$ is observed only near T_C. Recent quantitative measurement[9] shows that $I_s(2\mathbf{q})/I_s(\mathbf{q})$ is less than $\frac{1}{10}$, even in the very vicinity of T_C.

(b) In the case of the $(0,\bar{1},1)$ reflection, for example,

$$I_s(\pm\mathbf{q}_1)\gtrsim I_s(\pm\mathbf{q}_3)\gg I_s(\pm\mathbf{q}_2)\text{: in the } +\phi \text{ domain}\ , \tag{4a}$$

$$I_s(\pm\mathbf{q}_3)\gtrsim I_s(\pm\mathbf{q}_1)\gg I_s(\pm\mathbf{q}_2)\text{: in the } -\phi \text{ domain}\ . \tag{4b}$$

(c) The satellites are clearly observed for $(h,k,0)$ reflections in which $F_1=F_2$ is intrinsically satisfied. In the case of the $(0,1,\bar{1})$ reflection whose satellites were extensively studied in the present work, $F_1\simeq F_2$ is accidentally satisfied at just below T_C in the α phase.

The (**g**,**q**) dependence is a crucial key to understanding the modulated structure. We obtained relations similar to (b) and (c) for the satellites of more than 20 Laue spots.[6,7] All of them are reasonably explained by the following "configuration waves" (CW) model.

By a similar calculation to the thermal diffuse scattering,[21] we know that the satellite intensity is proportional to $[\mathbf{g}\cdot\mathbf{U}(\mathbf{q})][\mathbf{g}\cdot\mathbf{U}^*(\mathbf{q})]$, where

$$\mathbf{U}(\mathbf{q})=\sum_k f_k\mathbf{u}_k(\mathbf{q})\exp(2\pi i\,\mathbf{g}\cdot\bar{\mathbf{r}}_k)\ . \tag{5}$$

In this expression f_k, $\bar{\mathbf{r}}_k$, and $\mathbf{u}_k$ refer to the kth atom of the unit cell and they are the scattering factor, the mean position, and the Fourier component of the displacement, respectively. So far, no serious work has been done concerning what mode must soften on the basis of lattice dynamics. In the following analysis, however, it is enough to assume that three equivalent CW's, $\mathbf{U}(\pm\mathbf{q}_i)$, are excited equally in the IP. At this stage it does not matter whether the 1**q** or 3**q** model is taken, although the former model is very unlikely for several reasons, as discussed in Refs. 9 and 10.

Here, we shall explain the $(0\bar{1},1)$ reflection. In an earlier stage, without recognizing $\pm\phi$ domain structure, it was concluded naively that $\mathbf{U}(\mathbf{q})$ is transverse to the **q** vector within the c plane. Then, we could expect that

$$I_s(\pm\mathbf{q}_1)=I_s(\pm\mathbf{q}_3),\ I_s(\pm\mathbf{q}_2)=0\ , \tag{6}$$

which was a good first approximation to the observed relations (4). In fact, at this stage, we were observing a mixture of $\pm\phi$ domains. The detailed results (4) indicate that $\mathbf{U}(\mathbf{q})$ has a longitudinal component. Incidentally, the discrepancy between (4) and (6) is predominant only in the range (T_C, $T_C+0.4$ K), where the second-harmonic contribution $I_s(2\mathbf{q})$ also becomes recognizable.

We have compared similar experimental results for the satellite reflections around more than 20 Laue spots including the $(1,\bar{1},0)$ reflection with the 3**q** CW model, and the agreement is satisfactory.

IV. CONCLUDING REMARKS

Evidence from x-ray topographic observations shows that the IP is a thermodynamically stable phase,[6] and the satellite reflections indicate that the modulated structure is incommensurate.[5,16] In addition, the IP has a new domain structure characterized by $\pm\phi$ rotation of a set of

$\mathbf{q}_i$.[7] The observed $(\mathbf{g},\mathbf{q})$ dependence is reasonably explained by the 3**q** model of the configuration waves, $\mathbf{U}(\pm\mathbf{q}_i)$. The vector character of the modulated waves is crucially important. Since the structure factor is scalar by definition, any model like the microtwins one in which simply a spatial distribution of F_1 and F_2 is assumed, may not be acceptable. The optical transforms of electron micrographs may not be substituted for the real satellite reflection, either in electron or x-ray diffraction, because the phase information is lost in electron micrographs.

Apart from the main theme, it is worth mentioning that the satellite reflection was extremely sharp, provided that a single $\pm\phi$ domain from a good specimen was selected. The broadening was estimated to be less than a few minutes or better. The irregularity of the triangular arrays observed in electron micrographs, therefore, may afford a false impression of the experimentally attainable situation. In this context, the broadening of the satellite reflection near T_C reported in neutron diffraction[8] may also be misleading as to the nature of the modulated structure. In neutron diffraction, the specimen must be a mixture of $\pm\phi$ domains, and the crystal perfection is not well defined.

The above statements, of course, do not imply any objection to the experimental fact that the structures manifested by electron microscopy exist under a certain condition. It seems, however, desirable to have direct evidence to elucidate whether the triangular contrast is really due to microtwins or something else. Also, specification of the temperature conditions is desirable.

If one admits that the triangular pattern observed over a μm field really corresponds to the modulated structure observed with x-rays in the range of 1.8 K, the temperature gradient amounts to 10^4 K/cm. This value, and consequently the thermal strain, are enormously large. For this reason, the structure observed by electron microscopy might be either a transient one or any structure which could appear only in the region of super modulation (Sec. II C). It is also conceivable that the temperature range of the IP becomes extremely narrow under the inhomogeneous condition compared with the thermodynamically homogeneous case. Thin-film effects might be another possibility.

In any case, we believe that x-ray (neutron) diffraction and electron microscopy are looking at different structures under very different conditions. This view is particularly necessary when the phase which we are interested in can exist only in a narrow temperature range.

Finally, it is highly desirable to develop any phenomenological theory of the Landau type based on the experimental results obtained under thermodynamically homogeneous conditions.

ACKNOWLEDGMENT

We acknowledge Professor Y. Ishibashi for valuable discussion.

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