

Subsequent to the approximation given by equations (2) Zachariassen appends a further approximation. It is that (2) may be written

$$I = I' \exp[-\mu(x + y)] = I' A(\mu) \quad (19)$$

[Zachariassen's (1967) equation (41)]. Here  $A(\mu)$  is simply the absorption correction appropriate for the kinematic result. This approximation modifies the Zachariassen solution displayed in Fig. 2 in that the solution is normalized so that it agrees with the kinematic solution in the limit that  $\sigma$  is small. However, its justification is obscure. Zachariassen claims that it is appropriate unless absorption effects are large. In actuality equation (19) holds in the limit that  $\mu \gg \sigma$ , in which case absorption effects and scattering may be treated separately and there results the kinematic theory. Becker & Coppens develop a rather more involved treatment of the effect of absorption. However, it is evolved still within the context of their approximate solution to the transfer equations, and it appears to contain the conclusion that often the diffraction effects related to  $\sigma$  and  $\mu$  may essentially be treated separately.

It is probably still useful to retain clearly the distinction between primary and secondary extinction. That the coupling of the incident and diffracted

amplitudes, with specific phase relations, is a phenomenon describable by solutions to the transfer equations, appropriate only for the incoherent phenomenon of secondary extinction, seems unlikely.

Experimental tests that allow the identification of observed extinction as of either the primary or secondary variety should also be useful. A description of such a test will be the subject of a subsequent contribution.

It seems to this writer that the present state of the theory of secondary extinction is primitive. The calculations described here are intended to suggest that the appropriate point of departure for further quantitative insights into this phenomenon is the exact solution to the transfer equations given by Werner.

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## On the Co-existence of Structurally Different Regions in the Low–High-Quartz and Other Displacive Phase Transformations

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(Received 2 February 1981; accepted 13 October 1981)

*Dedicated to Professor Dr Heinz Jagodzinski on the occasion of his 65th birthday*

#### Abstract

The mechanism of the low  $\rightleftharpoons$  high quartz phase transformation is discussed in terms of tilting of  $[\text{SiO}_4]$  tetrahedra and formation of Dauphiné twin domains below the transformation temperature. The low-quartz domain boundaries have a finite thickness. Within the domain wall the tilt angle changes gradually from  $+\varphi$  to  $-\varphi$ . Depending on temperature, the gradual change may be static or there may be a change of the average

value of  $\varphi$  due to a dynamical process. Around the center of the wall between the low-quartz domains the structure resembles that of high quartz. The co-existence of low- and high-quartz-type regions in a temperature range below the transformation temperature is a necessary consequence of the formation of coherent domains. It is concluded that analogous ranges of coexistence of low- and high-symmetry regions exist in many, if not all, displacive phase transformations in which the phases involved have

subgroup–supergroup symmetry relations and, therefore, form twin domains (dielectric, ferroelastic phase transformations, *etc.*).

### Introduction

Within recent years the low  $\rightleftharpoons$  high phase transformation of quartz has been studied extensively with a number of experimental methods. Changes of mean atomic positions with temperature below and above the transformation temperature  $T_c$  of about 846 K have been determined by X-ray diffraction (Young, 1962) and neutron diffraction (Wright & Lehmann, 1981); the lattice dynamics of the transformation has been studied by IR and Raman spectroscopy (Scott, 1974), with thermal diffuse X-ray scattering (Arnold, 1976) and with inelastic neutron scattering (Axe & Shirane, 1970; Bauer, Jagodzinski, Dorner & Grimm, 1971; Boysen, Dorner, Frey & Grimm, 1980, among others). The dynamical process of reversible domain formation of low quartz has been observed by critical opalescence (Yakolev, Velichkina & Mikheeva, 1956; Shapiro & Cummins, 1968) and by electron microscopy (Malov & Sonyushkin, 1976; Van Tendeloo, Van Landuyt & Amelinckx, 1976); the coexistence of low and high quartz in a temperature range between  $T_c$  and approximately  $T_c - 1$  K has been deduced from fundamental and second-harmonic light scattering (Dolino & Bachheimer, 1977) and from measurements of the refractive index (Semenchenko, Bodnar & Fotchenkov, 1979).

According to classical thermodynamics, two phases that are related by a first-order transition coexist at  $T_c$  because they have the same Gibbs free energy  $G$  at this temperature. The stable coexistence of low and high quartz in a temperature interval, observed by Dolino & Bachheimer (1977), however, requires a corollary interpretation: either small impurities that change the transformation temperature produce a two-phase field, or the total Gibbs free energy must be described by some other term(s) in addition to the volume Gibbs free energy of the ideal crystal, *e.g.* a surface-energy term or a strain-energy term.

It will be discussed in this paper that coexistence of structurally different regions within a temperature range is not exceptional but rather has to be expected for displacive phase transformations in general.

### Mechanism of low $\rightleftharpoons$ high-quartz transformation

The low-quartz structure is built as a tetrahedral network in which the tetrahedra are joined in a double spiral with two nonintersecting threads around the trigonal axis. The rather rigid tetrahedra are tilted away from the symmetrical orientations shown in the bottom part of Fig. 1 about diad axes parallel to (100) by an

angle  $\varphi$  (Megaw, 1973). At room temperature the tilt angle is about  $16^\circ$ . Two states  $\alpha_1$  and  $\alpha_2$  of low quartz of the same enantiomorph (left or right handed) exist which are transformed into each other by a diad axis coinciding with the trigonal axis (Fig. 1). These two states correspond to Dauphiné twin domains which differ by tilt angles of opposite direction. Thus, at a given temperature, the tilt angle  $\varphi$  of each tetrahedron may have one of two different equilibrium values. It can be regarded as an order parameter, which changes sign upon transformation from state  $\alpha_1$  to the alternate state  $\alpha_2$ .

With increasing temperature the  $[\text{SiO}_4]$  tetrahedra change size and shape only very slightly. However, the oscillation of the rigid tetrahedra (*i.e.* of the tilt angle about its equilibrium value) is enhanced when the temperature is increased. This mode can be described as a strongly coupled libration of quasi-rigid tetrahedra along chains parallel to the axes [100], [010] and [110] (Fig. 2) which are interconnected to form a three-dimensional framework (Fig. 1). It is this cooperative motion within a chain of rigid tetrahedra which Grimm & Dorner (1975) reported to be involved in a soft mode at the  $\alpha \rightleftharpoons \beta$  transformation at about 843 K and which was also studied by Boysen *et al.* (1980).

With increasing temperature the amplitude of the thermal motion increases, whereas the average displacement of the oxygen atoms measured from the midpoint of the  $\alpha_1$ ,  $\alpha_2$  positions decreases; this displacement is correlated with  $\varphi$ , so the tilt angle

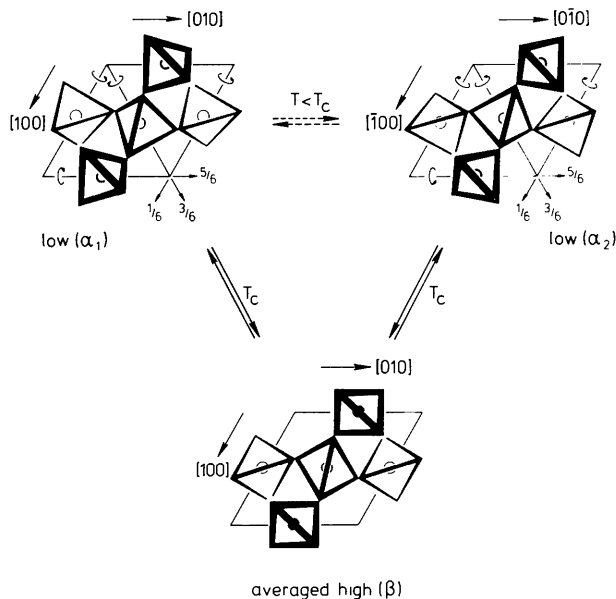


Fig. 1. Schematic representation of the average structure of high quartz ( $\beta$ -quartz) and of the structure of the two states  $\alpha_1$  and  $\alpha_2$  of low quartz of the same enantiomorph (right-handed quartz). The small curved arrows in the low-quartz diagrams indicate the sense of tilting of the tetrahedra about the diad axes.

decreases also. It is suggested by Megaw (1973) that the  $\alpha \rightleftharpoons \beta$  transformation occurs when the r.m.s. amplitude in the direction of the displacement becomes equal to the displacement. Megaw (1973) also suggested that in a temperature region below the transition temperature the low-quartz single crystal breaks up into small  $\alpha_1$ ,  $\alpha_2$  domains, which seem to be constantly shifting their boundaries and switching from one orientation to the other. These Dauphiné twin domains with strongly temperature-dependent fluctuations of the domain walls have been observed by Van Tendeloo *et al.* (1976) in the electron microscope. Low quartz, thus, consists of two equilibrium states  $\alpha_1$  and  $\alpha_2$ . An individual chain parallel to directions [100], [010] or [110] of the tetrahedra may be described as a particle in a double-minimum potential (positive or negative order parameter); it can be considered as being located in the left or in the right minimum respectively. When the temperature is raised the probability for a transition from state  $\alpha_1$  to state  $\alpha_2$  (and *vice versa*) is increased, which results in the observed formation of fluctuating domains just below the transformation. However, there is still some controversy about the structure of the hexagonal  $\beta$ -phase. Three models are conceivable:

(i) Above the transition temperature the structure relaxes to a midpoint position between  $\alpha_1$  and  $\alpha_2$ . The tilt angle  $\varphi$  is zero in this model, the double-minimum potential for each chain would degenerate to a one-minimum potential.

(ii) Near the transition temperature the above-mentioned pattern of Dauphiné twin domains is formed. Even above the transition temperature this domain pattern is maintained. The  $\beta$ -quartz structure is only a geometrical average of  $\alpha_1$ ,  $\alpha_2$  microdomains. Atoms inside the domains are distributed between two trigonal positions and atoms in the interface occupy hexagonal midpoint positions. This implies that each chain inside a domain occupies either of the two minima in a double-minimum potential; only the potential in the interface is reduced to one minimum.

(iii) Near to the transition temperature the chains start to fluctuate between the two permissible states  $\alpha_1$

and  $\alpha_2$ . This fluctuation increases when the temperature is raised above  $T_c$ . Below  $T_c$  such fluctuations are correlated, yielding microdomains. Above  $T_c$  the long-range correlation ceases; each chain fluctuates independently between the two minima in a double-minimum potential. The  $\beta$ -quartz structure can be conceived as both a geometrical and a time average of two equilibrium positions. At  $T_c$  there is a transition from a microdomain structure to the  $\beta$ -quartz structure of uncorrelated chain oscillations.

Model (i) was proposed by the classical work of Young (1962); model (ii) is favored by Boysen *et al.* (1980). The third model (iii) is promoted in this paper.

Arnold (1976) and Wright & Lehmann (1981) have shown by structure refinement calculations that  $\alpha_1$ ,  $\alpha_2$  split positions for the oxygen atoms have to be maintained above  $T_c$  to improve the  $R$  factor. This eliminates model (i). The displacement from the midpoint decreases with increasing temperatures only until transitions into the alternate state begin. The onset of such transitions is rather sudden because they are correlated with the motion of the neighboring chains; the transformation into such a domain structure is, possibly, of first order. The cooperative fluctuations between two equilibrium positions cause the formation of a periodic array of domains (Böhm & Roth, 1982). Thus the microdomain pattern (van Tendeloo *et al.*, 1976) is just an intermediate state, which according to Megaw (1973) 'smears out' the sharpness of the transition. The domain walls in such an array of  $\alpha_1$ ,  $\alpha_2$  microdomains determine the physical properties of this intermediate state and the course of the transformation; this will be discussed in the next section.

### Structure of the domain boundaries in low quartz

For Dauphiné twin domain boundaries of zero thickness the misfit between the structures of the two neighboring domains would create considerable stress at the interface. Since the lattices of the two domains are coherent this stress at the interface is reduced by a strained domain wall of finite thickness. This means that at low temperatures, when no activation energy is available to overcome the energy barrier between the two minima of the potential curve (Fig. 3,  $T \ll T_c$ ), the tilt angle does not switch abruptly from  $+\varphi$  to  $-\varphi$  when passing through the interface but rather changes continuously. Therefore, at the center of the wall the potential is expected to have a minimum at the midpoint of the  $\alpha_1$ ,  $\alpha_2$  positions. Because of the considerable strain energy only coarse  $\alpha_1$ ,  $\alpha_2$  domains are found at room temperature. These might be stabilized by defects.

As the temperature is raised close to the transition temperature  $T_c$  microdomains are formed due to correlated fluctuations between the two equilibrium

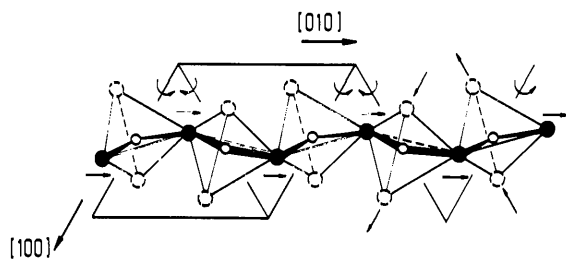


Fig. 2. Schematic representation of the cooperative libration along a chain of quasi-rigid tetrahedra. The curved arrows indicate the sense of tetrahedral tilt, the small straight arrows the horizontal component of shift of the oxygen atoms away from the average position in high quartz.

positions. Within a domain wall, transitions of an individual chain having a positive tilt angle  $+\varphi$  to one having a negative tilt angle  $-\varphi$  (and *vice versa*) are likely to happen more often than in the center of a domain. For any chain of tetrahedra in the wall with, say,  $+\varphi$  there is a considerable force from the adjacent domain having a tilt angle  $-\varphi$ , which may induce transitions into the alternate state; they cause the domain wall to fluctuate. In the middle of the wall there is a 50% chance of finding an individual chain of tetrahedra in either position (Fig. 3,  $T \lesssim T_c$ ). The average tilt angle should be zero at such a position; the average is to be taken over both space (along the domain wall) and time. Therefore, the center of the domain wall exhibits the  $\beta$ -phase structure as described in model (iii) (Fig. 3,  $T > T_c$ ). In other words, in the intermediate state of correlated fluctuations structurally different regions of low and high quartz coexist (Fig. 3,  $T \lesssim T_c$ ).

It depends very much on the experiment and the probe used whether an average in space or in time is observed. The transitions between the two equilibrium states are expected to occur with phonon frequencies or even more slowly; a geometrical average is therefore obtained in most experiments. In a scattering experiment with X-rays [ $t \sim 1$  as ( $= 10^{-18}$  s)], for instance, a geometrical average of the range of coherence is 'seen' by the photon, *i.e.* in the domain wall both states appear to be occupied equally. This is even true if the range of coherence comprises several  $\alpha_1$ ,  $\alpha_2$  microdomains. Only if one microdomain becomes larger than the range of coherence should the occupancy of one state (*e.g.*  $\alpha_1$ ) prevail.

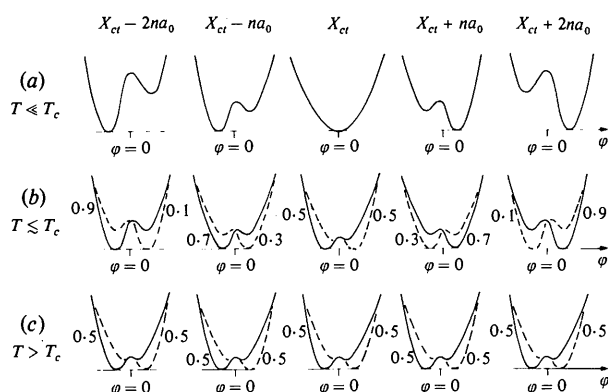


Fig. 3. Hypothetical variation of the potential (averaged in space along the domain wall and in time) of a chain of quasi-rigid tetrahedra within a domain wall of thickness  $4na_0$  between neighboring  $\alpha_1$ - and  $\alpha_2$ -state domains of quartz at different temperatures. (a)  $T \ll T_c$ ; (b)  $T \lesssim T_c$ ; (c)  $T > T_c$ . For each temperature the potential is plotted *versus* the tilt angle  $\varphi$  for five different values of the space coordinate  $X$ . ( $X_{ct}$  = space coordinate at the center of the domain wall.) The numbers refer to the occupancy of the corresponding potential.

If, instead, the refractive index of light is studied, the corresponding values for both coexisting states should be observed. Semenchenko *et al.* (1979) found an overlap region of about 0.7 K at the  $\alpha \rightleftharpoons \beta$  transition of natural quartz, where the refractive indices of both low and high quartz could be observed simultaneously. This should correspond to a temperature range where  $\alpha_1$ ,  $\alpha_2$  microdomains and domain walls ( $\beta$ -quartz) coexist in comparable volume portions. In the process of the transformation the volume of the domain walls is increased until the  $\alpha_1$ ,  $\alpha_2$  microdomains have disappeared. The refractive index experiment obviously supports model (iii) rather than (ii).

In Fig. 4 the variation of the tilt angle across the domain wall is shown schematically. At low temperatures it may represent the continuous variation of  $\varphi$  due to the stress. At higher temperatures below  $T_c$  it may be regarded as the most probable angle at this particular position in the domain wall, *i.e.* as an average value  $\langle \varphi \rangle$ . The change in space and with time of the tilt angle of the tetrahedra in the domain walls of low quartz is analogous to the changes of the orientations of dipole moments in domain boundaries of ferroelectric substances.

## Discussion

The  $\alpha \rightleftharpoons \beta$  transformation in quartz is characterized by an intermediate state of correlated fluctuations. They bring forth microdomains, which are Dauphiné twins of low quartz. Individual chains of tetrahedra perform transitions into the other permissible twin state in the domain walls more often than in the center of the domain. These transitions imply that the average tilt angle becomes zero. In the domain wall, therefore, a structure of high quartz is realized which is an average in space and time of two equilibrium states that are occupied by individual chains of rigid tetrahedra librating cooperatively. However, it depends on the

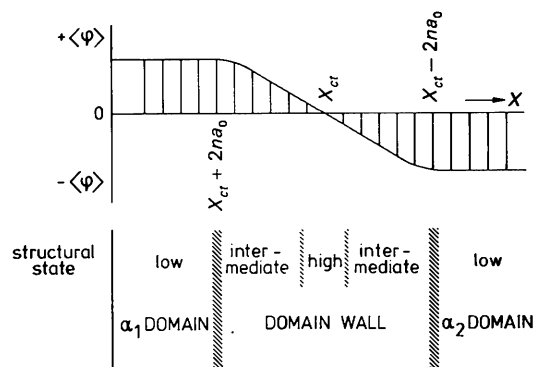


Fig. 4. Change of the average tilt angle  $\langle \varphi \rangle$  of  $[\text{SiO}_4]$  tetrahedra within a domain wall of thickness  $4na_0$  between neighboring  $\alpha_1$ - and  $\alpha_2$ -state domains of low quartz ( $X_{ct}$  = space coordinate at the center of the domain wall.)

geometrical resolution of the experiment and on the time scale used in the method whether both coexisting states of low and high quartz are detected simultaneously.

As the temperature approaches  $T_c$  from below, the size of the low-quartz domains approaches zero so that the volume portion of domain walls increases and the amount of high-quartz-type regions within the walls with it.

From these considerations it follows that the coexistence of low- and high-quartz-type regions in a temperature range below the transformation temperature is a necessary consequence of the formation of Dauphiné twin domains in quartz.

As there is a continuous change from the low-quartz-type region to the high-quartz-type region when passing from the interior of a domain to the center of the domain wall below  $T_c$ , these regions cannot be considered to be two distinct phases in the sense of classical thermodynamics since such phases would have to be separated by an interface at which the physical properties change discontinuously. The term 'coexistence' applied to low- and high-quartz-type regions is therefore used here in its ordinary linguistic usage and does not imply stable coexistence of thermodynamic phases in terms of volume properties.

The low  $\rightleftharpoons$  high-quartz transformation is just one example from the large class of displacive phase transformations in which the low-temperature phase is a distorted version of a more symmetrical high-temperature structure and where the relationship between the space-group symmetries of both phases is that between subgroup and supergroup. In all these phase transformations single crystals of the high-temperature phase transform into twins of the low-temperature phase during cooling, since the low-temperature phase exhibits two or more energetically equivalent equilibrium states. In contrast, heating single crystals of the low-temperature phase to temperatures just below their transformation temperatures produces twin domains by a process similar to that in quartz.

Some examples of this class of phase transformations are: Low  $\rightleftharpoons$  high cristobalite,  $\text{SiO}_2$  (Peacor, 1973); low  $\rightleftharpoons$  intermediate  $\rightleftharpoons$  high tridymite,  $\text{SiO}_2$  (Kihara, 1978); low  $\rightleftharpoons$  high titanite,  $\text{CaTi}[\text{SiO}_4]\text{O}$  (Taylor & Brown, 1976); dielectric phase transformations, e.g. orthorhombic  $\rightleftharpoons$  tetragonal  $\rightleftharpoons$  cubic

$\text{BaTiO}_3$  (Schildkamp & Fisher, 1981); ferroelastic phase transformations, e.g. triclinic  $\rightleftharpoons$  monoclinic  $\rightleftharpoons$  orthorhombic  $\rightleftharpoons$  tetragonal  $\rightleftharpoons$  cubic  $\text{CsPbCl}_3$  (Alexandrov, Besnosikov and Posdnjakova, 1976).

As a consequence of the domain formation below the transformation temperature, in many (if not all) displacive transformations with subgroup-supergroup symmetry relations coexistence of corresponding high- and low-temperature regions in the sense described in this paper has to be expected below  $T_c$ .

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