Theory of domain structures and associated defects in the incommensurate phase of quartz

M. B. Walker*
Institut Laue-Langevin, 156X, 38042 Grenoble Cédex, France
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Two distinct sets of domain walls having the same free energy are predicted to exist in quartz; each set has its own triangular domain structure, which differs in orientation from that of the other set, and this gives rise to the possibility of a macrodomain structure in quartz. The question of the nature of the interface between two macrodomains is raised. The various possibilities for connecting the domain walls in both sets together give rise to the possibility of a large number of different defect structures.

A triangular domain structure in the transition region between the high-temperature β phase and the low-temperature α phase has been observed in quartz by dark-field-imaging electron microscopy by van Tendeloo *et al.*[1,2] The observed dark and bright domains were identified as Dauphiné twins. The purpose of this paper is to consider theoretically, in terms of a phenomenological free energy introduced by Aslanyan and Levanyuk,[3] the possible relative orientations of the domain walls separating two Dauphiné twins, and hence to account for the observed domain structures and the possible defects in these domain structures. My considerations concerning the domain-wall orientation are closely related to the wave-vector-orientation considerations of Aslanyan *et al.*[4] The latter have shown that the model[3] allows (within mean-field theory) a second-order phase transition from the high-temperature β phase to the incommensurate phase, and that the incommensurate wave vector, which is along the a^* direction at the transition temperature, gradually rotates away from the a^* direction as the temperature is lowered. However, an original contribution of the present paper is the recognition of a twofold degeneracy in the domain-wall orientation, so that one has two distinct sets of domain walls (the φ_+ and φ_- walls described below); this has significant implications for the possible domain geometries. In addition a detailed description of the possible domain configurations is given below.

A basal-plane projection of the positions of the silicon ions in a unit cell of quartz is shown in Fig. 1. The arrows show the directions of the displacements undergone by the silicon ions in the transition from the β phase to the α phase. The order parameter η of the phase transition can be taken to have a magnitude equal to the magnitude of the displacement of a given silicon ion, and is positive if the displacement is in the direction indicated and negative if the displacement is in the opposite direction. The so-called Dauphiné twins correspond to the fact that η can be either positive or negative. An excellent review of the properties of the α-β phase transition in quartz is that of Dolino and Bachheimer.[5]

In the incommensurate phase of quartz, the order parameter $\eta(\vec{x})$ is inhomogeneous (in this paper $\vec{x}$ is a two-dimensional vector in the basal plane, the crystal being assumed to be homogeneous in the c-axis direction). The model free energy of Aslanyan and Levanyuk can be written

$$F=F_\beta+\sum_{\vec{k}}\{A+[C_1+C_2\cos^2(3\varphi)]k^2+Dk^4\}\,|\,\eta_{\vec{k}}\,|^2 + \int d^2x\left\{\tfrac{1}{4}B\eta^4+G\left[\left[\frac{\partial\eta}{\partial x}\right]^3-3\left[\frac{\partial\eta}{\partial x}\right]\left[\frac{\partial\eta}{\partial y}\right]^2\right]\right\}, \tag{1}$$

where the wave vector $\vec{k}$ is in the basal plane and makes an angle φ with the x axis defined in Fig. 1; F_β is the free energy of the β phase. The term proportional to C_2 is a nonanalytic term in $\vec{k}$ and has been shown[3,4] to arise as a result of the interaction of the order parameter with the strain field. This term could be replaced by, or supplemented by, an analytic term proportional to $k^6\cos^2(3\varphi)$, which has the same angular dependence, without affecting the arguments of the present paper.

In this paper it will be assumed that planar domain walls between Dauphiné twins do exist under the appropriate conditions, as indicated by the electron microscopy results.[1,2] An order parameter describing a planar domain wall normal to the x' axis of Fig. 1 has the form

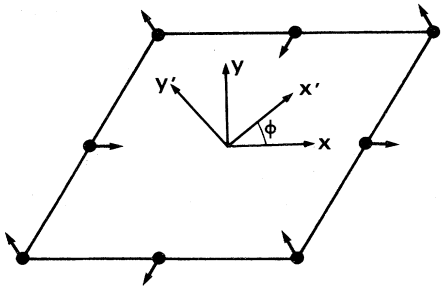

FIG. 1. Basal-plane projections of the position of the silicon ions in the quartz structures. The solid circles give the silicon positions in the β phase, whereas the arrows give the directions of the silicon displacements in the transition to the α phase. The directions of the x,y and x',y' coordinate axes are also defined by this figure.

$$\eta(\vec{x})=\eta(x') , \tag{2}$$

i.e., it is a function of the variable x' only. With the assumption of Eq. (2), the free energy becomes

$$F=F_\beta+\int dx' \left[\tfrac{1}{2}A\eta^2+[C_1+C_2\cos^2(3\varphi)]\left[\frac{d\eta}{dx'}\right]^2 +D\left[\frac{d^2\eta}{dx'^2}\right]^2+G\cos(3\varphi)\left[\frac{d\eta}{dx'}\right]^3 +\tfrac{1}{4}B\eta^4\right] . \tag{3}$$

The electron microscope studies[1,2] have concluded that the domain walls are parallel to the x axis (or its equivalent) of Fig. 1 within experimental error, and the published,[6] as well as more recent,[7] neutron scattering results (which show that the incommensurate wave vectors are along the y axis or equivalent directions) support this conclusion. It will therefore be assumed that φ is sufficiently close to the $\frac{1}{2}\pi$ that the terms in $\cos(3\varphi)$ and $\cos^2(3\varphi)$ in (3) can be neglected initially, and the departure of φ from $\frac{1}{2}\pi$ will be determined later by perturbation theory. This assumption will be true for our model provided C_2 is positive and the magnitude of the ratio G/C_2 is sufficiently small. Now let the function $\eta(x')$, which minimizes F [with $\cos(3\varphi)=0$ and $A<0$], subject to the boundary conditions

$$\eta(\pm\infty)=\pm\eta_0=\pm(|A|/B)^{1/2} ,$$

be called $\eta_w(x')$. It is assumed that some such function exists and has a shape as indicated qualitatively in Fig. 2. It should be noted that if $\eta_w(x')$ minimizes the free energy for $\cos(3\varphi)=0$, then $\eta_{w'}(x')\equiv\eta_w(-x')$ does also. The free energy of Eq. (3) is now minimized with respect to $\cos(3\varphi)$ with $\eta(x')$ being given the value $\eta_w(x')$, the result being

$$\cos(3\varphi_+)=-\frac{G}{C_2}\frac{\int(d\eta_w/dx')^3dx'}{\int(d\eta_w/dx')^2dx'} . \tag{4}$$

The zero-order solution $\eta_{w'}(x')$ yields a domain wall with the same energy as the one just considered, but with an orientation angle $\varphi=\varphi_-$ given by $\cos(3\varphi_-)=-\cos(3\varphi_+)$. The angles φ_+ and φ_- can be written in the form

$$\varphi_\pm=\tfrac{1}{2}\pi\pm\epsilon+\tfrac{2}{3}\pi n , \tag{5}$$

where ϵ is a small positive angle and $n=0,\pm1$ [these solutions for φ_- are in fact also present in Eq. (4)].

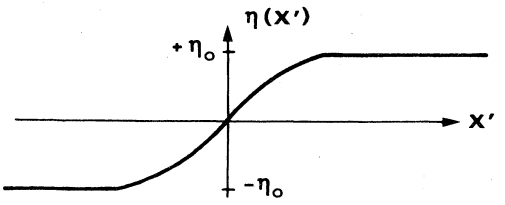

FIG. 2. Qualitative behavior of the order parameter at a domain wall.

There are thus two distinct sets of domain walls, which will be called the φ_+ walls and the φ_- walls, respectively. The three walls in a given set make angles of $\frac{2}{3}\pi$ with respect to each other, whereas the domain walls of the φ_+ set are rotated relative to those of the φ_- set by the angle 2ϵ. The φ_- and φ_+ sets of domain walls are illustrated pictorially in Figs. 3(a) and 3(b). All of the walls have the same energy, a result which follows from symmetry arguments as well as the detailed calculations given above. For example, the y axis of Fig. 1 is a twofold symmetry axis of the β phase, and relates each domain wall of Fig. 3(a) with a wall of Fig. 3(b).

One consequence of Figs. 1(a) and 1(b) is that it is not possible to form a stripe phase[8] in which stripes of $\eta=+\eta_0$ and $\eta=-\eta_0$ alternate as one crosses the basal plane.

It will be useful, for the purpose of making a detailed analysis of the electron microscope images of the domain configurations, to have an idea of what different kinds of domain-wall configurations are possible on theoretical grounds. When a domain wall is crossed there is no change in the position or orientation of the crystallographic unit cell (as is the case in 2H-$TaSe_2$, for example[9]) and there is, therefore, nothing to restrict the possible connec-

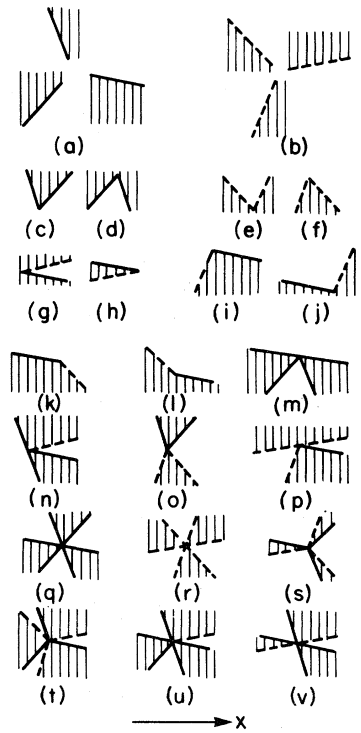

FIG. 3. Three φ_- domain walls are shown in (a) and the φ_+ domains walls are shown in (b); the shaded and unshaded regions on either side of a domain wall correspond to $\eta=+\eta_0$ and $\eta=-\eta_0$, respectively. Parts (c)—(l) show two-wall intersections; the angles of intersection of the walls are (c) $\frac{1}{3}\pi$, (d) $\frac{1}{3}\pi$, (e) $\frac{1}{3}\pi$, (f) $\frac{1}{3}\pi$, (g) 2ϵ, (h) 2ϵ, (i) $\frac{2}{3}\pi-2\epsilon$, (j) $\frac{2}{3}\pi-2\epsilon$, (k) $\frac{2}{3}\pi+2\epsilon$, (l) $\frac{2}{3}\pi+2\epsilon$. Four-wall intersections are shown in (n)—(p), and six-wall intersections are shown in (q)—(v). The direction of the x axis, as defined in Fig. 1, is shown at the bottom.

tions of the domain walls other than the fact that on a given side of a domain wall of a given orientation, the sign of η is not arbitrary, but is given by Figs. 1(a) and 1(b). Thus only vertices at which two, four, or six walls intersect are possible. Figures 1(c)—1(e), plus the intersections tions obtained by rotating these by $\pm 2\pi/3$, give all possible twofold intersections. Fourfold and sixfold intersections can be obtained by combining twofold intersections in various ways, and an arbitrary selection of each is shown in the remaining parts of the figure. The intersection of Fig. 3(m) has been observed in quartz by van Tendeloo *et al.*[1,2] The usefulness of a table of basic intersections is that an arbitrary domain structure will be found to be some combination of them.

A triangular domain structure can be formed using only the φ_- domain walls, and only the sixfold intersection of Fig. 3(q) and this is shown in the upper half of Fig. 4. This upper half of Fig. 4 is the basic domain structure observed by van Tendeloo *et al.*[1,2] However, it should be noted that a second triangular domain structure made up out of φ_+ walls and the sixfold intersection of Fig. 3(r) is possible. This second structure is shown in the bottom half of Fig. 4 and can be seen to be obtained from the structure in the top half by a rotation about the c axis of $\pi+2\epsilon$. It would thus appear to be possible to have a "macrodomain" structure in quartz (a region in which the walls are exclusively φ_- walls, such as the top half of Fig. 4, will be called a φ_- macrodomain). Figure 4 also shows how an interface between a φ_- macrodomain and a φ_+ macrodomain could be formed using a number of different intersections; this is only one possibility and it would be of interest to study electron microscope images of such an interface in detail (provided, of course, that the existence of such interfaces can be confirmed).

It is also of interest to consider the mechanism of the phase transition from the incommensurate phase to the α phase. This transition is accomplished by eliminating domain walls from the incommensurate phase. In principle, if the transition is thermodynamically continuous, this could be done by a continuous expansion of the triangular structure with the loss of domain walls at the sample surfaces, although pinning of the domain walls at lattice defects or at the surfaces could inhibit this process. Alternatively, one can imagine the process shown in Fig. 5 occurring, in which one of the triangular domains collapses (over some activation energy barrier) with the loss of three domain walls. The above arguments indicate that

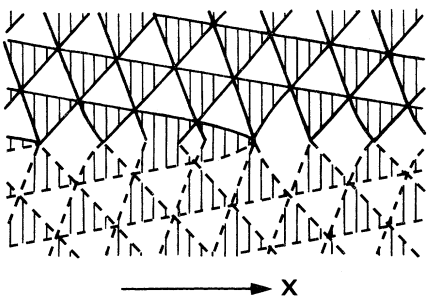

FIG. 4. Possible interface between a φ_- macrodomain at the top, and a φ_+ macrodomain at the bottom.

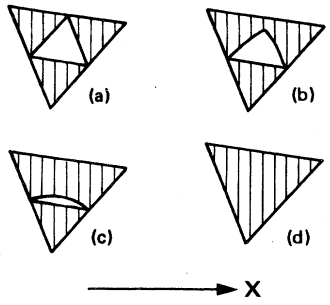

FIG. 5. Possible mechanism for removing domain walls from a crystal during the transition from the incommensurate phase to the α phase; a triangular domain can collapse as shown in (a)—(d).

it will be difficult to determine experimentally whether or not the phase transition is thermodynamically continuous, since even if it is thermodynamically continuous, it would be expected to be hysteretic.

To conclude, notice that this work has deduced a picture of the triangular domain structure and of a particular defect in this structure [that of Fig. 3(m)], both of which have been observed by electron microscopy studies by van Tendeloo *et al.*,[1,2] and has laid down a basis for examining a wide variety of other defect structures.

I have been informed[10] that recent unpublished electron microscopy studies of quartz carried out by G. van Tendeloo, J. van Landuyt, and S. Amelinkx have produced two observations which are not accounted for by existing theoretical work. The first is that there is sometimes embedded in a large region having a regular triangular domain structure a smaller region whose domain walls make angles of approximately 20° with those of the larger region. Such an observation is simply accounted for in the present work by the assumption that the larger region is a φ_+ macrodomain and the smaller region is a φ_- macrodomain, or vice versa. This would indicate that the angle ϵ introduced above is approximately 10°. The second observation is that there exist domains which are not equilateral triangles, but which are more like isosceles triangles, with two sides longer than the third. This observation can also be accounted for within the framework of the present work if one notes the possibility of forming triangles of which one of the vertices is as shown in Figs. 3(g) or 3(h).

Further detailed analyses of electron micrographs are necessary to determine whether or not the above considerations are fully consistent with the observed structures and also to determine, for example, the nature of the actual interfaces between the φ_+ and φ_- macrodomains, of which Fig. 4 is intended only as a stimulative, speculative example. Investigations of the processes occurring in the incommensurate to α-phase transition, a representative possibility of which is shown in Fig. 5, would also be of interest.

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*Permanent address: Department of Physics and Scarborough College, University of Toronto, Toronto, Ontario M5S 1*A* 7 Canada.

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