Properties of Dauphiné-twin domain walls in quartz and berlinite

M. B. Walker and R. J. Gooding
Department of Physics and Scarborough College, University of Toronto, Toronto, Ontario, Canada M5S 1A7
(Received 18 April 1985)

The Dauphiné-twin domain walls in quartz and berlinite are shown to be ferroelectrically polarized, and the relative directions of the polarization vector in the six different orientations of domain walls are determined. Furthermore, a discontinuity in the displacement field is shown to occur at a domain wall, and vertices at which domain walls intersect are shown to be associated with dislocations in the strain field; these dislocations are characterized by their Burgers vectors.

INTRODUCTION

In attempting to elucidate the mechanism of the α-β transition in quartz and in berlinite ($AlPO_4$), Van Tendeloo *et al.*[1] discovered the regular triangular Dauphiné-twin domain structure which is characteristic of the incommensurate phase of these materials and which exists in only a very small temperature interval in between the α and β phases (for quartz this temperature interval is[2] approximately 1.3 K). They also observed a coarse Dauphiné-twin domain structure in the α phase. More detailed electron microscopy studies[3,4] and neutron-diffraction studies[2,3] of these Dauphiné-twin structures have become available recently.

Theoretical interpretations of the incommensurate phase of quartz have been given independently by Aslanyan *et al.*[5] and by Walker[6] in terms of the same Ginzburg-Landau—model[7] free energy, but using different methods of analysis. The analysis of Aslanyan *et al.*[5] was carried out in terms of the three fundamental spatial Fourier components of an order parameter describing a periodic domain structure, whereas Walker[6] proceeded by first establishing the orientational properties of the domain walls. The domain-wall picture can be used not only to interpret the incommensurate phase, but also to interpret the wide variety of different domain configurations which occur during the first-order commensurate-incommensurate phase transition, and to interpret the domain walls occurring in the coarse domain structure observed[1] in the α phase. A detailed investigation confirming the applicability of the domain-wall model to a wide variety of situations has been given by Van Landuyt *et al.*[4]

In this article we discuss both the electric polarization and the strains associated with the Dauphiné-twin domain walls. Dolino[8] has reported the results of theoretical calculations by M. Vallade and B. Berge, following the approach of Ref. 5, showing that the incommensurate phase of quartz should be ferroelectric, even though both the α and β phases are not. Here we examine the ferroelectricity of the incommensurate phase in terms of the domain-wall picture and show that it is the domain walls themselves which carry the electric polarization.

This results allows a discussion not only of the electric polarization of the incommensurate phase itself, but of the various domain-wall defect structures which occur during the incommensurate-to-α-phase change of phase, and also of the residual domain walls giving rise to the coarse Dauphiné-twin structure observed in the α phase. We also study the strains induced in quartz by the Dauphiné-twin domain walls and show that a discontinuity in the displacement occurs when a domain wall is crossed.

POLARIZATION PROPERTIES

The phase transition from the β to the α phase in quartz is a structural phase transition as a result of which the ions undergo displacements as shown in Fig. 1.[9] A similar transition occurs in berlinite.[10] The order parameter η for 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 displacements are in the direction indicated, and negative if the displacements are in the opposite direction. The so-called Dauphiné-

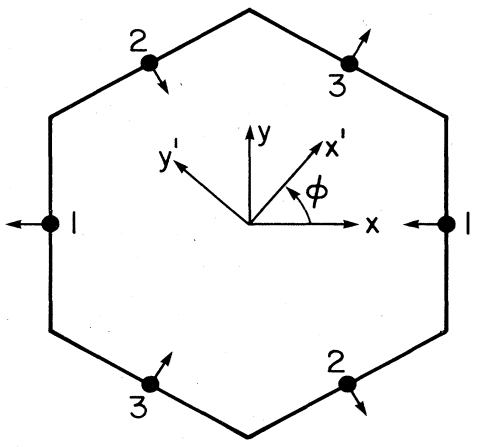

FIG. 1. Basal-plane projection of the positions of the silicon ions in the Wigner-Seitz cell of the quartz structures. The solid circles give the silicon positions in the β phase, whereas the arrows give the directions of the silicon displacements in the transition to the α phase. The directions of the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

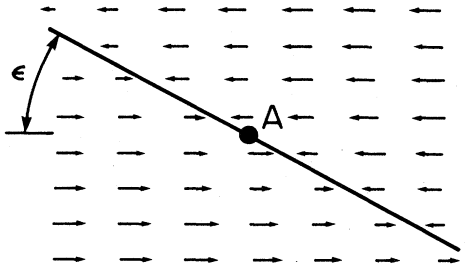

FIG. 2. Basal-plane projection of the silicon-ion displacements in the neighborhood of a domain wall separating a Dauphiné twin corresponding to $\eta=+\eta_0$ in the upper part of the figure from a twin corresponding to $\eta=-\eta_0$ in the lower part. The displacements of the silicon ions labeled 1 in Fig. 1 are indicated by arrows in the figure and are parallel to the x axis of Fig. 1; the displacements of the silicon ions labeled 2 and 3 in Fig. 1 are omitted for the sake of simplicity. The solid circle labeled A is the basal-plane projection of a twofold rotation axis of symmetry of the figure: this twofold axis is parallel to the c axis and is contained in the domain wall (the solid line).

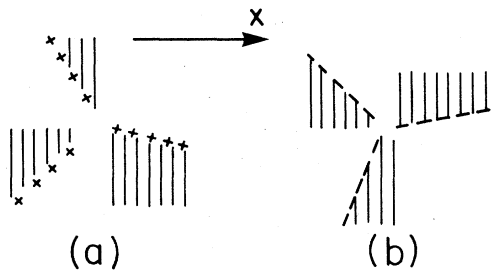

FIG. 3. Basal-plane projections of the three ϕ_+ domain walls and of the three ϕ_- domain walls are shown in (a) and (b), respectively. The shaded and unshaded regions on either side of a domain wall correspond to the Dauphiné twin having $\eta=-\eta_0$ and $\eta=+\eta_0$, respectively, and the direction of the x axis defined in Fig. 1 is also shown. The macroscopic polarization associated with each domain wall will give rise to a bound surface charge density when the domain wall terminates at a crystal surface; the domain walls are thus indicated schematically by a line of plus or minus signs indicating the relative sign of the surface charge density produced by the walls.

twins, which appear as dark or bright domains in the electron micrographs, correspond to the fact that η can be either positive or negative.

A section of a quartz crystal containing a domain wall between the two Dauphiné twins is illustrated schematically in Fig. 2. Notice that the axis labeled A, which is normal to the plane of the paper, is a twofold axis of symmetry of this crystal. Clearly, any basal-plane component of the electric dipole moment of this crystal must vanish, otherwise the crystal would not have the twofold symmetry axis just mentioned. There is no symmetry which requires the c-axis component of the electric dipole moment to vanish, however, and this component of the dipole moment must therefore be nonzero in general. Since the point-group symmetry of the α phase is D_3 there can be no spontaneous electric dipole moment of the α phase, as is well known, and the electric dipole moment of this crystal which we have been discussing must therefore be associated with the domain wall.

There are six different orientations of domain walls in quartz,[6] as shown in Fig. 3. Since the three ϕ_+ domain walls are related by threefold rotations about the c axis, all have the same electric dipole moment per unit area directed in the same sense. The ϕ_- walls are obtained from the ϕ_+ walls by appropriate twofold rotations about an axis lying in the basal plane and these walls are therefore polarized in the opposite sense to the ϕ_+ walls.

Similar conclusions concerning the polarization of the domain walls can also be obtained by extending the phenomenological model to include the coupling of the order parameter to the electric polarization. The appropriate terms in the free energy per unit volume for a description of the z component of the electric polarization are

$$F=a(P_z)^2+P_z\{b(\eta_{yyy}-3\eta_{xxy})+c[\eta_x(\eta_{xxy}+\eta_{yyy})-\eta_y(\eta_{xxx}+\eta_{xyy})]+d(\eta_y^3-3\eta_x^2\eta_y)$$
$$+e\eta(\eta_y\eta_{yy}-\eta_y\eta_{xx}-2\eta_x\eta_{xy})+f\eta^2(\eta_{yyy}-3\eta_{xxy})\}\ , \tag{1}$$

where a subscript coordinate attached to η indicates a derivative with respect to that coordinate (although P_x, P_y, and P_z are the x, y, and z components of the electric polarization vector). Now if the total free energy is minimized with respect to P_z, and η is assumed to be a function of the variable x' only (see Fig. 1), as is appropriate for the case of a planar domain wall,[6] one finds

$$P_z=(2a)^{-1}\sin(3\phi(b\eta_{x'x'x'}+d\eta_{x'}^3+e\eta\eta_{x'}\eta_{x'x'}$$
$$+f\eta^2\eta_{x'x'x'})\ . \tag{2}$$

The total dipole moment of the wall per unit area is thus

$$\mathcal{P}_z=(2a)^{-1}\sin(3\phi)(d+\tfrac{1}{2}e+f)\int_{-\infty}^{\infty}dx'\,\eta_{x'}^3\ . \tag{3}$$

For a domain wall, η and $\eta_{x'}^3$ are shown schematically in Fig. 4; clearly, $\mathcal{P}_z$ is nonzero unless $\phi=2\pi n/3$. Considered as a function of ϕ, this dipole moment has its maximum magnitude for ϕ close to $(\pm\frac{1}{2}+\frac{2}{3}n)\pi$, which

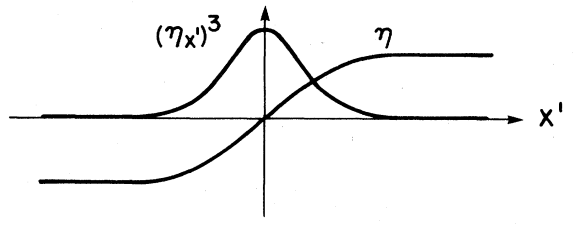

FIG. 4. Qualitative behavior of the order parameter and the cube of its first derivative as a function of x' in the neighborhood of a domain wall.

corresponds approximately to the observed orientation of the domain walls in quartz and berlinite. If the order parameter is sufficiently small, which will be the case at temperatures sufficiently close to the incommensurate-to-β-phase transition temperature, the term proportional to b in Eq. (2) will give the largest contribution to the position-dependent polarization, although it oscillates in sign and makes no contribution to the macroscopic polarization of Eq. (3).

A similar analysis for the components P_x and P_y of the polarization gives

$$F=h(P_x^2+P_y^2)+j[P_x(\eta_{xx}-\eta_{yy})-2P_y\eta_{xy}]+k\eta(P_x\eta_x+P_y\eta_y)+l\eta[P_x(\eta_{xxx}+\eta_{xyy})+P_y(\eta_{xxy}+\eta_{yyy})]$$
$$+m\{P_x[\eta_x(\eta_{xx}-\eta_{yy})+2\eta_y\eta_{xy}]-P_y[\eta_y(\eta_{xx}-\eta_{yy})-2\eta_x\eta_{xy}]\} \quad (4)$$

for the free-energy density, and

$$P_x=-(2h)^{-1}[j\cos(2\phi)\eta_{x'x'}+\cos\phi(k\eta\eta_{x'}+l\eta\eta_{x'x'x'}+m\eta_{x'}\eta_{x'x'})]\,, \quad (5)$$

$$P_y=(2h)^{-1}[j\sin(2\phi)\eta_{x'x'}-\sin\phi(k\eta\eta_{x'}+l\eta\eta_{x'x'x'}+m\eta_{x'}\eta_{x'x'})]\,. \quad (6)$$

Integrating P_x and P_y with respect to x' gives zero, as required by the symmetry argument given above. Thus, nonzero P_x and P_y are also produced in the wall and these quantities oscillate in sign and average to zero. These quantities have a nonzero divergence and produce a nonzero bound charge density in the crystal.

STRAIN FIELD PROPERTIES

The lowest-order contributions to the free-energy density which involve the strains and the coupling of the strain to the order parameter are[7]

$$F=\frac{K}{2}(e_{xx}+e_{yy})^2+\frac{\mu}{2}[(e_{xx}-e_{yy})^2+4e_{xy}^2]$$
$$+\frac{a}{2}[(e_{xx}-e_{yy})\eta_x-2e_{xy}\eta_y]\,, \quad (7)$$

where the definition of the strain fields e_{ij} in terms of the displacement field $u_i (i=x,y)$ is

$$e_{ij}=\frac{1}{2}\left[\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right]. \quad (8)$$

Minimizing the free energy with respect to the inhomogeneous displacement field and assuming that all quantities are functions of the variable x' only (see above and Fig. 1), we find

$$u_x=\frac{-a\eta}{\mu(\mu+k)}\left[\left(\frac{K}{2}+\mu\right)\cos(2\phi)-\frac{K}{2}\cos(4\phi)\right], \quad (9)$$

$$u_y=\frac{-a\eta}{\mu(\mu+K)}\left[\left(\frac{K}{2}+\mu\right)\sin(2\phi)+\frac{K}{2}\sin(4\phi)\right], \quad (10)$$

where the arbitrary constants in the solution are chosen so that $u_i=0$ at the center of a domain wall where $\eta=0$.

Now consider a domain wall for which $\phi=(\pi/2)-\epsilon$, with ϵ small. (At low temperatures in the α phase ϵ has approximately the values 9° and 5° in quartz and berlinite, respectively; ϵ decreases in magnitude in the incommensurate phase as the temperature is raised towards the incommensurate-to-β-phase transition[4].) In the approximation $\epsilon \ll 1$, this wall is nearly parallel to the xz plane and the displacement of the underlying lattice on crossing the wall in the x' direction is

$$\Delta u_{x'}=\frac{2a\eta_0}{\mu}\left[\frac{2K-\mu}{K+\mu}\right]\epsilon\,, \quad (11)$$

$$\Delta u_{y'}=-\frac{2a\eta_0}{\mu}+\frac{2a\eta_0}{\mu}\left[\frac{7K+\mu}{K+\mu}\right]\epsilon^2 \quad (12)$$

to order ϵ^2 where η_0 is the magnitude of the order parameter far from a domain wall. The effect of such a displacement is shown for two of the walls of Fig. 3 in Fig. 5, where ϵ is considered so small that the contribution $\Delta u_{x'}$ in (11) can be neglected; the displacement field discontinuities for the remaining four walls are obtained by rotating these figures by $\pm(2\pi/3)$ about an axis normal to the page. The principal effect of a domain wall (oriented at an angle near those found in quartz and in berlinite) is thus to introduce a shearing of the lattice, although some volume change in the region of the domain wall will also occur and will be relatively more important for larger ϵ.

In quartz and berlinite, vertices at which two, four, or six walls intersect are possible. An example of vertex at which two walls intersect is shown in Fig. 6. A closed-circuit C circling the vertex, as in Fig. 6, crosses each of the walls joined to V. When crossing the ith wall, the dis-

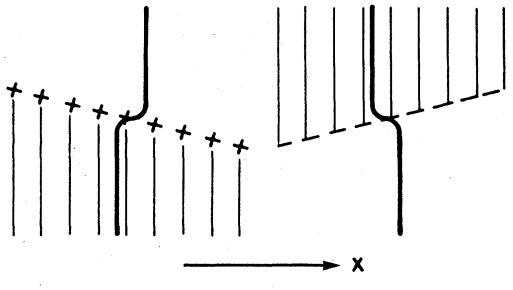

FIG. 5. Two of the domain walls of Fig. 3 are shown again in (a) and (b), respectively. The extra-heavy solid lines represent scratches on the (basal-plane) surface of the crystal which, in the absence of the domain wall, would be straight lines. The shearing effect of the walls on the lattice is clearly evident. The x direction is as defined in Fig. 1.

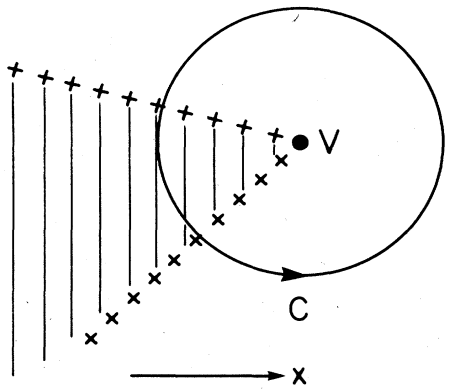

FIG. 6. The vertex V formed by the intersection of two of the ϕ_+ walls shown in Fig. 3(a). The Burgers circuit is labeled C and the direction of the x axis is as defined in Fig. 1.

placement field undergoes a discontinuity $\Delta\mathbf{u}_i$, so that the total discontinuity undergone in a complete circuit around the vertex V is

$$\mathbf{b}_V=\sum_i \Delta_i \ . \tag{13}$$

Thus, the vertex V behaves like an edge dislocation characterized by the Burgers vector $\mathbf{b}_V$. The regular six-line vertices from which the triangular domain structure of the incommensurate phase is formed [these are shown in Figs. 3(q) and 3(r) of Ref. 6] are special cases for which $\mathbf{b}_V=0$, but many types of vertices exist which, like that of Fig. 6, have $\mathbf{b}_V$ not equal to zero. The total Burgers vector (which is the sum of the Burgers vectors of all of the vertices) is conserved whenever a change in the domain configuration occurs.

CONCLUSIONS

The Dauphiné-twin domain walls in quartz possess a nonzero spatial-average electric polarization along the c-axis, with all three ϕ_+ domain walls being polarized in the same sense, this being opposite to the common sense of polarization of the ϕ_- domain walls. In addition to a nonzero spatial-average electric polarization, which varies as the cube of the order parameter, the domain walls carry a contribution to the electric polarization which averages to zero as a result of its oscillations in sign as one crosses a domain wall, but which varies as the first power of the order parameter. This oscillating contribution should be much larger than the spatial-average contribution at temperatures close to the incommensurate-to-β-phase transition temperature.

In the incommensurate phase of quartz, one observes[7] a macrodomain structure in which there are two types of macrodomains.[5,6] The ϕ_+ macrodomain is a triangular domain structure made up entirely of ϕ_+ domain walls and, hence, carrying a total ferroelectric polarization in the same sense as that of the ϕ_+ walls; the triangular domain structure of a ϕ_- macrodomain is made up from ϕ_- domain walls and carries a ferroelectric polarization in the opposite sense to that of a ϕ_+ macrodomain.

It is interesting to note that the interfaces between the two types of Dauphiné twins which are observed in the α phase consist generally of alternating ϕ_+ and ϕ_- domain walls.[4] Clearly, one should be unsuccessful in attempting to move such interfaces by applying an inhomogeneous electric field since the electrical forces on the ϕ_+ and ϕ_- walls would be in opposite directions. Many other domain geometries can be identified and analyzed in terms of the ϕ_+ and ϕ_- domain walls,[4] and the relative electric polarizations of these domain walls can be determined by reference to Fig. 3 above.

The displacement field was shown to undergo a discontinuity on crossing a domain wall. Furthermore, domain wall vertices were shown to be associated with dislocations in the strain field, and the Burgers vectors of these vertices were identified.

ACKNOWLEDGMENTS

This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). R. J. Gooding acknowledges the partial support of NSERC.

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