Ferroelastic domain walls in $\text{Hg}_2\text{Br}_2$ and KSCN

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Abstract. The quantitative analysis of the properties of domain walls in $\text{Hg}_2\text{Br}_2$ and KSCN is performed using the Landau–Ginzburg phenomenological description. The domain walls in KSCN are thin and possess high internal stresses in comparison with $\text{Hg}_2\text{Br}_2$. The interactions between domain walls have opposite characters in the two materials.

1. Introduction

The properties of domain walls (DWS) with finite thickness have been theoretically investigated in several materials, e.g. in the perovskite crystals $\text{BaTiO}_3$ [1–3] and $\text{SrTiO}_3$ [4, 5], in the ferroelectric $\text{TGS}$ [6], in $\text{Gd}_2(\text{MoO}_4)_3$ [7] and recently also in the improper ferroelectrics $\text{Hg}_2\text{Br}_2$ and KSCN [8]. The common feature in all cases is the appearance of inhomogeneous deformations and corresponding stresses localized around the centre of the wall. It is the consequence of a gradual variation of the structure and the matching conditions for the position-dependent strain tensor. A considerable part of the surface free energy can have its origin in the above-mentioned deformations. The internal strains also influence the orientations of non-ferroelastic DWS, i.e. the angular dependence of the surface free energy. On the contrary the orientations of the ferroelastic domain walls (FDWS) are completely determined by the deformation of the bulk domains separated by the wall.

In our previous paper we have studied the antiphase boundaries (APBS) in $\text{Hg}_2\text{Br}_2$ and KSCN [8]. The angular dependences of the wall characteristics—the surface free energy, the position-dependent strains and stresses, and the thickness—were calculated for the linear structure of the APB. Contrary to KSCN, the APB in $\text{Hg}_2\text{Br}_2$ was shown to be unstable and to split into two FDWS. Our aim in this paper is to study the properties of FDWS in the two materials. The profiles of the FDWS are calculated and the interactions between two parallel FDWS are also discussed.

Let us state now that in the analysis of the FDWS we shall with advantage use some of results derived for the generally oriented quasi-one-dimensional structures in [8]. Therefore we shall only briefly repeat the method and the details can be found in [8]. In both crystals under consideration the tetragonal-to-orthorhombic phase transitions are described by the two-component order parameter (OP) $p$, $q$. The OP is related to the spontaneous displacements of $\text{Hg}_2\text{Br}_2$ molecules and the ordering of $\text{SCN}^-$ dipoles. The free-energy density expansion $f$ involves four terms [8]:

$$f = f_0 + f_e + f_c + f_g$$

(1)

\dagger The zero value of the angle $\phi$ introduced in [8] corresponds to the orientation of the compatible FDW.
where \( f_0 \) contains the primary OP only, \( f_s \) represents the coupling between the OP and the strain, \( f_e \) is the elastic part of the free energy and \( f_g \) is the gradient term. The equilibrium conditions for the quasi-one-dimensional structure of the \( uv \) perpendicular to the \( x \) axis are

\[
\frac{\partial}{\partial \xi} \left( \frac{\partial f}{\partial p} \right) - \frac{\partial f}{\partial p} = 0
\]

(2a)

\[
\frac{\partial}{\partial \xi} \left( \frac{\partial f}{\partial q} \right) - \frac{\partial f}{\partial q} = 0
\]

(2b)

\[
\sigma_1 = \sigma_3 = \sigma_5 = 0.
\]

(2c)

The stress components \( \sigma_i \) are given by the formulae

\[
\sigma_i = \frac{\partial f}{\partial u_{i}}, \quad i = 1, \ldots, 6
\]

(3)

where \( u_i \) are strain tensor components. In a material without defects the matching rules of the strain tensor also have to be satisfied. In the case of the layered structure perpendicular to the \( x \) axis they have the simple form

\[
u_2(x) = u_{2s} \quad u_3(x) = u_{3s} \quad u_4(x) = u_{4s}
\]

(4)

where \( u_{2s}, u_{3s}, \) and \( u_{4s} \) are position-independent quantities. This means that the deformations parallel to the wall plane are required to be constant over all the space. For the homogeneous stress-free crystal the spontaneous deformations can be derived from equations (2) [8]:

\[
u_{2s} = u_{1s} = l_1(p_s^2 + q_s^2)
\]

\[
u_{3s} = l_3(p_s^2 + q_s^2) \quad u_{6s} = l_6(p_s^2 - q_s^2)
\]

\[
u_{4s} = u_{5s} = 0
\]

(5)

where the spontaneous values \( p_s \) and \( q_s \) minimize the reduced free energy.

\[
\hat{f} = \frac{1}{2} \alpha (p^2 + q^2) + \frac{1}{4} \beta (p^4 + q^4) + \frac{1}{2} \gamma p^2 q^2.
\]

(6)

The reduced free energy (6) follows from (1) by substituting the strain components (5). For \( \gamma > \beta > 0 \) the four stable domain states are

\[
1_1: \quad p_s = -p_0 \quad q_s = 0 \quad u_{6s} = +l_6 p_0^2
\]

(7a)

\[
1_2: \quad p_s = +p_0 \quad q_s = 0 \quad u_{6s} = +l_6 p_0^2
\]

\[
2_1: \quad p_s = 0 \quad q_s = +p_0 \quad u_{6s} = -l_6 p_0^2
\]

(7b)

\[
2_2: \quad p_s = 0 \quad q_s = -p_0 \quad u_{6s} = -l_6 p_0^2
\]

where \( p_0 = \sqrt{-\alpha/\beta} \). The ferroelastic domain states 1 and 2 possess shear stresses of opposite signs. Let us note that the strain components \( u_2, u_3 \) and \( u_4 \) parallel to the wall plane have the same values \( u_{2s}, u_{3s} \) and \( u_{4s} \) in two ferroelastic domains, e.g. \( 1_1 \) and \( 2_1 \). Then the conditions (4) are fulfilled and the bulk domains fit together along the \( y-z \) plane. This FDW (notation \( 1_1-2_1 \)) is compatible according to Sapriel [9]. Nevertheless, the stresses will appear around the wall plane because of the gradually changing structure.
2. Ferroelastic domain walls

In the case of the FWD 1\textsubscript{1}–2\textsubscript{1} the perpendicular to the $x$ axis the system of equations (2)–(4) should be solved with the boundary conditions

$$
p(\xi = -\infty) = -p_0 \quad p(\xi = +\infty) = 0
$$

$$
q(\xi = -\infty) = 0 \quad q(\xi = +\infty) = p_0.
$$

The position-independent strain components $u_2$, $u_3$, and $u_4$ have the spontaneous values $u_2s$, $u_3s$, and $u_4s$, respectively, according to compatibility conditions (4). The remaining components can depend on the position $x$ and the corresponding expressions are

$$
u_1(x) = u_{1s} - (l'_1/c_{11})(p^2(x) + q^2(x) - p_0^2)
$$

$$
u_6(x) = -(l'_6/c_{66})(p^2(x) - q^2(x))
$$

$$
u_5(x) = 0.
$$

The coupling coefficients $l'_i$ between the strains and the OP are defined in [8]; $c_{ij}$ are the elastic constants. The stress components, which are necessary to keep the deformations (4) constant, are

$$
s_2(x) = (l'_1/(c_{11} - c_{12}))/c_{11})(p^2(x) + q^2(x) - p_0^2)
$$

$$
s_3(x) = (l'_3 - l'_1/c_{33}/c_{11})(p^2(x) + q^2(x) - p_0^2)
$$

$$
s_4(x) = 0.
$$

By substituting the strains (9) into the free energy (1), one can derive the reduced free energy [8]

$$
f = \frac{1}{2} u^* (p^2 + q^2) + \frac{1}{4} \beta^* (p^4 + q^4) + \frac{1}{2} \gamma^* p^2 q^2 + \frac{1}{2} g[(\partial_x p)^2 + (\partial_x q)^2]
$$

where $\alpha^* = \alpha + 2p_0^2(-2\Lambda + l'_1/c_{11} + l'_6/c_{66})$, $\beta^* = \beta' - 2(l'_3/c_{11} + l'_6/c_{66})$, and $\gamma^* = \gamma' - \beta' - 2(l'_3/c_{11} - l'_6/c_{66})$; $\Lambda$ is the determinant of the matrix $c_{ij}$.

The position-dependent OP $p(x), q(x)$ is the solution of the Lagrange–Euler equations

$$
g \partial_{\xi}^2 p = \alpha^* p + \beta^* p^3 + \gamma^* p q^2
$$

$$
g \partial_{\xi}^2 q = \alpha^* q + \beta^* q^3 + \gamma^* q p^2
$$

with the boundary conditions (8). Equations (12) and (8) can be solved in a special case only, when $\gamma^* = 3\beta^*$ [4, 10, 11]:

$$
p(x) = \frac{1}{2} p_0[-1 + \tanh(Kx)]
$$

$$
q(x) = \frac{1}{2} p_0[1 + \tanh(Kx)]
$$

$$
K = \sqrt{-\alpha^*/2g}.
$$

This case corresponds to the multicritical point [11]. Then the interaction between two FDWs $1_1–2_1$ and $2_1–1_2$ is zero and the surface free energy $\sigma_{APB}$ of the APB equals twice the free energy $\sigma_{FDW}$ of the FWD. Such FDWs do not interact at all. They can move independently in the crystal or annihilate and create the APB $1_1–1_2$. Since $q(x) - p(x) = p_0$, the contour
of (13) in the OP space is the straight line in figure 1. The profile (13) can be used as an approximation for $\gamma^* \neq 3\beta^*$. By using (13) and integrating (11) the surface free energy of FDW is

$$\sigma_{\text{FDW}} = \frac{(5\beta^* + \gamma^*)p_0^2}{24K} = \frac{4}{3} |F_0| d_{\text{FDW}} \frac{\beta^*}{\beta} \left( \frac{1}{2} + \frac{\gamma^* - 3\beta^*}{16\beta^*} \right)$$  \tag{14}

where $F_0 = -\beta p_0^4/4$ is the free-energy density of the homogeneous domain and the thickness of FDW follows from (13):

$$d_{\text{FDW}} = 2/K.$$  \tag{15}

According to [8] the APB thickness $d_{\text{APB}} = d_{\text{FDW}}$, and the expression outside the parentheses is the surface free energy $\sigma_{\text{APB}}$ of the APB. Then we rewrite (14) in the instructive form

$$\sigma_{\text{FDW}} = \sigma_{\text{APB}} \left( \frac{1}{2} + \frac{\gamma^* - 3\beta^*}{16\beta^*} \right).$$  \tag{16}

One can easily see that $2\sigma_{\text{FDW}} < \sigma_{\text{APB}}$ for $\gamma^* - 3\beta^* < 0$. In this case the APB splits into two FDWs, which repulse each other [11]. If $\gamma^* - 3\beta^* > 0$, then the interaction between FDWs is attractive [11], and the energetically more favourable APB is stable.

![Figure 1. Contours of FDWs in the OP space: ---, approximate contour corresponding to the profile (13).](image)

The other possibility is the approximation of the constant radius based on the assumption of the arc contour $p^2(x) + q^2(x) = p_0^2$ [12]. Let us note that the deviation of the exact contour in the OP space from the circle of radius $p_0$ controls the values of the strain $u_1(x)$ and the stresses $\sigma_2(x), \sigma_3(x)$ (see equations (9) and (10)).

3. Hg$_2$Br$_2$ and KSCN

The values of the free-energy expansion coefficients and the elastic constants are known for both crystals under consideration [8]. In the following we assume the temperature $T = T_c - 5$ K. The profiles of FDWs were numerically calculated by the relaxation method [10] for both materials (figure 2). The corresponding contours in the OP space are depicted in figure 1. One can see (figure 2) that equation (13) provides a good approximation since
q(x) - p(x) deviates only slightly from the constant value. In Hg₂Br₂, γ* < 3β*.
Then the APB 1₁-2₁ is unstable and splits into two FDWs 1₁-2₁ and 2₁-1₂. These two FDWs
repulse each other. The surface free energy \( \sigma_{FDW} = 0.47\sigma_{APB} = 0.008 \text{ erg cm}^{-2} \), where
\( \sigma_{APB} = 0.018 \text{ erg cm}^{-2} \) [8]. As mentioned above, \( 2\sigma_{FDW} < \sigma_{APB} \). Note that the contour
has a convex shape.

On the contrary, γ* > 3β* in KSCN. Then the contour has a concave shape and
the interaction between FDWs 1₁-2₁ and 2₁-1₂ is attractive. In agreement with this the
APB 1₁-2₁ is stable and \( 2\sigma_{FDW} > \sigma_{APB} \), where \( \sigma_{FDW} = 0.56\sigma_{APB} = 0.26 \text{ erg cm}^{-2} \)
and \( \sigma_{APB} = 0.47 \text{ erg cm}^{-2} \) [8]. By using (15) the thickness of the FDW is about 320 Å (i.e.
70 lattice constants) for Hg₂Br₂ and about 26 Å (i.e. four lattice constants) for KSCN. The
position-dependent components of the stress are shown in figures 3 and 4. In Hg₂Br₂ the
maximum value of \( \sigma_3 \) is nearly 0.2 MPa and the amplitude of \( \sigma_3 \) is less than 0.1 MPa. The
maximum values of stress are two orders of magnitude higher in KSCN, namely 35 MPa
for \( \sigma_2 \) and 8 MPa for \( \sigma_3 \). The minus sign of the stress components indicates that the central
region of the DW is prevented from expanding parallel to the FDW plane, i.e. it is compressed.

It is interesting to estimate the increase in the free energy due to the deformations.
Let us remove the restrictions of compatibility conditions. This corresponds to cutting the
crystal into layers perpendicular to the x axis, which are allowed to relax freely. Then
the homogeneous part of the free energy (11) is replaced by (6). The difference between
the real value $\sigma_{FDW}$ and the free energy of such a partitioned crystal has its origin in the inhomogeneous deformations. This increase in the free energy represents only 0.5% in Hg$_2$Br$_2$, but 43% in KSCN. To discuss this difference let us note that the percentage for an APB depends on its orientation and varies between 0% and 42% in Hg$_2$Br$_2$ (where the zero value corresponds to the APB parallel to the FDW), while it is always above 55% in KSCN [8]. From the quantitative estimation of $l_1$ and $l_0$ in equations (5) it can be shown that the elementary cell of KSCN below $T_c$ shrinks along all directions, while elongation and contraction of the cell along the principal strain tensor axis occur in Hg$_2$Br$_2$. Consequently, in the latter case an appropriately oriented APB can be found (approximately parallel to the FDW), along which the domains fit the central disordered part of APB without large strains [7]. This is impossible in KSCN. The difference between the FDWs of the two materials has, naturally, the same origin. Note that our explanation is not based on the microscopic structure.

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