Ferroelastic domain walls in Hg_2Br_2 and KSCN

1994 J. Phys.: Condens. Matter 6 11159

(http://iopscience.iop.org/0953-8984/6/50/023)

J. Phys.: Condens. Matter 6 (1994) 11159–11165. Printed in the UK

Ferroelastic domain walls in Hg_2Br_2 and KSCN

I Rychetsky† and W Schranz‡

† Institute of Physics, Czech Academy of Sciences, Na Slovance 2, 18040 Prague, Czech Republic

‡ Institut für Experimentalphysik, Universität Wien, Strudlhofgasse 4, 1090-Wien, Austria

Received 14 February 1994, in final form 6 September 1994

Abstract. The quantitative analysis of the properties of domain walls in Hg_2Br_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 Hg_2Br_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 $BaTiO_3$ [1–3] and $SrTiO_3$ [4, 5], in the ferroelectric TGS [6], in $Gd_2(MoO_4)_3$ [7] and recently also in the improper ferroelastics Hg_2Br_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 (FWDs) 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 Hg_2Br_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 Hg_2Br_2 was shown to be unstable and to split into two FDWs. Our aim in this paper is to study the properties of FWDs 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 Hg_2Br_2 molecules and the ordering of SCN^- dipoles. The free-energy density expansion f involves four terms [8]:

$$f = f_o + f_c + f_e + f_g \tag{1}$$

† The zero value of the angle ϕ introduced in [8] corresponds to the orientation of the compatible FDW.

0953-8984/94/5011159+07$19.50

where f_0 contains the primary OP only, f_c 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 DW perpendicular to the x axis are

$$\frac{\partial}{\partial \zeta}\left(\frac{\partial f}{\partial p_\zeta}\right) - \frac{\partial f}{\partial p} = 0 \tag{2a}$$

$$\frac{\partial}{\partial \zeta}\left(\frac{\partial f}{\partial q_\zeta}\right) - \frac{\partial f}{\partial q} = 0 \tag{2b}$$

$$\sigma_1 = \sigma_5 = \sigma_6 = 0. \tag{2c}$$

The stress components σ_i are given by the formulae

$$\sigma_i = \frac{\partial f}{\partial u_i} \qquad i = 1, \ldots, 6 \tag{3}$$

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

$$u_2(x) = u_{2s} \qquad u_3(x) = u_{3s} \qquad u_4(x) = u_{4s} \tag{4}$$

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]:

$$\begin{aligned} &u_{2s} = u_{1s} = l_1(p_s^2 + q_s^2) \\ &u_{3s} = l_3(p_s^2 + q_s^2) \qquad u_{6s} = l_6(p_s^2 - q_s^2) \\ &u_{4s} = u_{5s} = 0 \end{aligned} \tag{5}$$

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

$$f = \tfrac{1}{2}\alpha(p^2 + q^2) + \tfrac{1}{4}\beta(p^4 + q^4) + \tfrac{1}{2}\gamma p^2 q^2. \tag{6}$$

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

$$\begin{aligned} &1_1\colon\ p_s = -p_0 \qquad q_s = 0 \\ &1_2\colon\ p_s = +p_0 \qquad q_s = 0 \end{aligned} \qquad u_{6s} = +l_6 p_0^2 \tag{7a}$$

$$\begin{aligned} &2_1\colon\ p_s = 0 \qquad q_s = +p_0 \\ &2_2\colon\ p_s = 0 \qquad q_s = -p_0 \end{aligned} \qquad u_{6s} = -l_6 p_0^2 \tag{7b}$$

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_1–2_1 the perpendicular to the x axis the system of equations (2)–(4) should be solved with the boundary conditions

$$\begin{aligned} &p(\zeta = -\infty) = -p_0 \qquad p(\zeta = +\infty) = 0 \\ &q(\zeta = -\infty) = 0 \qquad q(\zeta = +\infty) = p_0. \end{aligned} \tag{8}$$

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

$$\begin{aligned} u_1(x) &= u_{1s} - (l_1'/c_{11})[p^2(x) + q^2(x) - p_0^2] \\ u_6(x) &= -(l_6'/c_{66})[p^2(x) - q^2(x)] \\ u_5(x) &= 0. \end{aligned} \tag{9}$$

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

$$\begin{aligned} \sigma_2(x) &= [l_1'(c_{11} - c_{12})/c_{11}][p^2(x) + q^2(x) - p_0^2] \\ \sigma_3(x) &= (l_3' - l_1'c_{33}/c_{11})[p^2(x) + q^2(x) - p_0^2] \\ \sigma_4(x) &= 0. \end{aligned} \tag{10}$$

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

$$f = \tfrac{1}{2}\alpha^*(p^2 + q^2) + \tfrac{1}{4}\beta^*(p^4 + q^4) + \tfrac{1}{2}\gamma^* p^2 q^2 + \tfrac{1}{2}g[(\partial_x p)^2 + (\partial_x q)^2] \tag{11}$$

where $\alpha^* = \alpha + 2p_0^2(-2\Lambda + l_1'^2/c_{11} + 1_6'^2/c_{66})$, $\beta^* = \beta' - 2(l_1'^2/c_{11} + 1_6'^2/c_{66})$ and $\gamma^* = \gamma' - \beta' - 2(l_1'^2/c_{11} - 1_6'^2/c_{66})$; Λ is the determinant of the matrix c_{ij}.

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

$$\begin{aligned} g\partial_{\xi\xi}^2 p &= \alpha^* p + \beta^* p^3 + \gamma^* p q^2 \\ g\partial_{\xi\xi}^2 q &= \alpha^* q + \beta^* q^3 + \gamma^* q p^2 \end{aligned} \tag{12}$$

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

$$\begin{aligned} p(x) &= \tfrac{1}{2}p_0[-1 + \tanh(Kx)] \\ q(x) &= \tfrac{1}{2}p_0[1 + \tanh(Kx)] \qquad K = \sqrt{-\alpha^*/2g}. \end{aligned} \tag{13}$$

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 σ_{APB} of the APB equals twice the free energy σ_{FDW} of the FDW. 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

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

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):

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

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

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

One can easily see that $2\sigma_{\mathrm{FDW}} < \sigma_{\mathrm{APB}}$ 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.

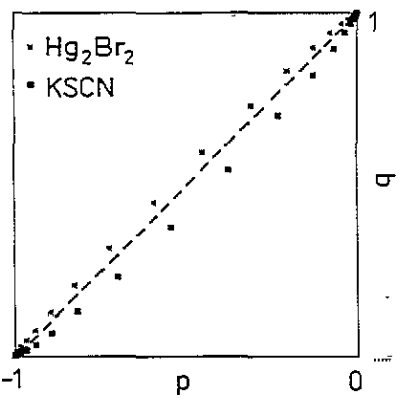

Figure 1. Contours of FDWs in the OP space: – – –, approximate contour corresponding to the profile (13).

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_2Br_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

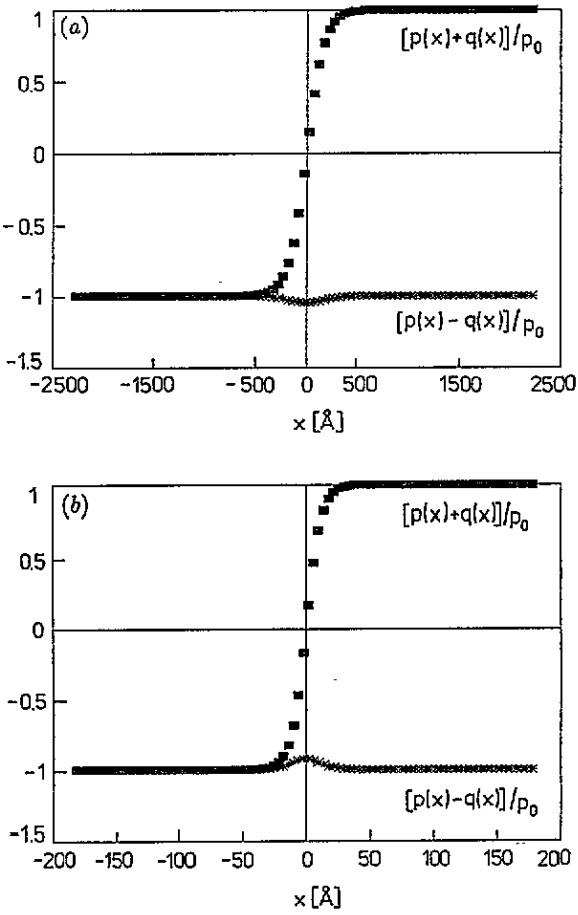

Figure 2. (*a*) Profile of FDW in Hg_2Br_2. Note that $p(x) - q(x) \simeq p_0$ and the approximation by (13) is reasonable. (*b*) The position-dependent OP in KSCN. The approximation $p(x) - q(x) \simeq p_0$ is reasonable.

$q(x) - p(x)$ deviates only slightly from the constant value. In Hg_2Br_2, $\gamma^* < 3\beta^*$. Then the APB 1_1–1_2 is unstable and splits into two FDWs 1_1–2_1 and 2_1–1_2. These two FDWs repulse each other. The surface free energy $\sigma_{FDW} = 0.47\sigma_{APB} = 0.008$ erg cm^{-2}, where $\sigma_{APB} = 0.018$ erg cm^{-2} [8]. As mentioned above, $2\sigma_{FDW} < \sigma_{APB}$. Note that the contour has a convex shape.

On the contrary, $\gamma^* > 3\beta^*$ in KSCN. Then the contour has a concave shape and the interaction between FDWs 1_1–2_1 and 2_1–1_2 is attractive. In agreement with this the APB 1_1–1_2 is stable and $2\sigma_{FDW} > \sigma_{APB}$, where $\sigma_{FDW} = 0.56\sigma_{APB} = 0.26$ erg cm^{-2} and $\sigma_{APB} = 0.47$ erg cm^{-2} [8]. By using (15) the thickness of the FDW is about 320 Å (i.e. 70 lattice constants) for Hg_2Br_2 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 Hg_2Br_2 the maximum value of σ_2 is nearly 0.2 MPa and the amplitude of σ_3 is less than 0.1 MPa. The maximum values of stress are two orders of magnitude higher in KSCN, namely 35 MPa for σ_2 and 8 MPa for σ_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

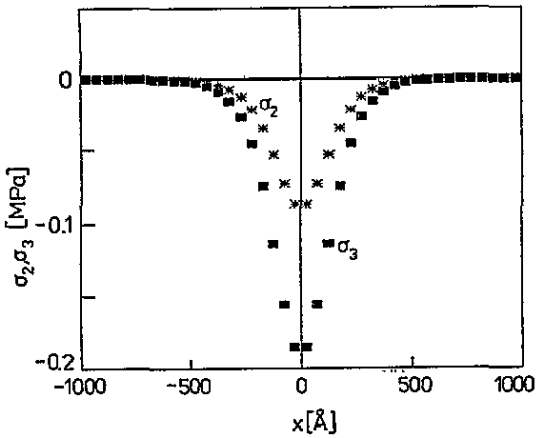

Figure 3. The position-dependent stresses in the FWD of Hg_2Br_2.

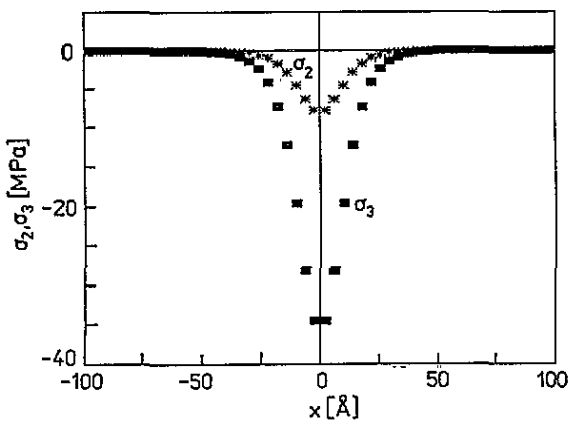

Figure 4. The position-dependent stresses in the FDW of KSCN.

the real value σ_{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_2Br_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_2Br_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_6 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_2Br_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.

Acknowledgments

This work has been supported by the Grant Agency of the Academy of Sciences of the Czech Republic under grant 11074 and the Österreicheischen Fonds zur Förderung der wissenschaftlichen Forschung unter project P 8285.

References

[1] Zhirnov V A 1958 *Zh. Eksp. Theor. Fiz.* **35** 1175 (Engl. transl. 1959 *Sov. Phys.–JETP* **35** 822)
[2] Bulaevskii L N and Ginzburg V L 1963 *Zh. Eksp. Teor. Fiz.* **45** 722 (Engl. transl. 1964 *Sov. Phys.–JETP* **18** 530)
[3] Dvorak V and Janovec V 1965 *Japan. J. Appl. Phys.* 4 400
[4] Cao W and Barsch G R 1990 *Phys. Rev.* B **41** 4334
[5] Cao W, Barsch G R and Krumhansl J A 1990 *Phys. Rev.* B **42** 6396
[6] Fousek J 1967 *Japan. J. Appl. Phys.* **6** 950
[7] Rychetsky I 1991 *J. Phys.: Condens. Matter* **3** 7117
[8] Rychetsky I and Schranz W 1993 *J. Phys.: Condens. Matter* **5** 1455
[9] Sapriel J 1975 *Phys. Rev.* B **12** 5128
[10] Ishibashi Y and Dvorak V 1976 *J. Phys. Soc. Japan* **41** 1650
[11] Sonin E B and Tagancev A K 1989 *Ferroelectrics* **98** 291
[12] Fouskova A and Fousek J 1975 *Phys. Status Solidi* a **32** 213