Domain wall diffusion and domain wall softening

W T Lee[1,2]**, E K H Salje**[2] **and U Bismayer**[1]

[1] Mineralogisch-Petrographisches Institut, Universität Hamburg, Grindelallee 48,
20146 Hamburg, Germany
[2] Department of Earth Sciences, University of Cambridge, Downing Street,
Cambridge CB2 3EQ, UK

E-mail: wlee@esc.cam.ac.uk

Abstract
A number of experimental and computational studies of materials have shown
that transport rates in domain walls may significantly differ from those in the
bulk. One possible explanation for enhanced transport in a domain wall is that
the domain wall is elastically soft with respect to the bulk. We investigate the
softening of a ferroelastic domain wall in a simple, generic model. We calculate
saddle point energies of solute atoms in the bulk and domain wall, using a
geometry such that variation in the saddle point energy cannot be attributed to
the structural differences of the bulk and the wall, but must instead be attributed
to softening of the wall. Our results show a reduction of the saddle point
energy in the wall, thus indicating that, in this model at least, domain walls are
elastically soft compared with the bulk. A simple analysis based on an Einstein
model allows us to explain the observed softening of the wall.

1. Introduction

It has recently been shown that diffusion in domain walls can be quite different from that in the
bulk of a material [1–4]. Experiments on the diffusion of sodium into WO_3 have shown that
the sodium ions diffuse much faster in the domain walls than in the bulk [1, 2]. A simulation of
diffusion of sodium parallel to the c-axis of quartz has shown that the diffusion in the domain
wall is significantly slower than in the bulk [4].

Many technologically important materials get their useful properties from phase transitions
and thus have domain walls. Furthermore the domain wall structure of these devices can be
controlled quite accurately by techniques such as lithography [9]. If these materials show fast
diffusion down domain walls then the domain walls can be selectively doped, confining the
dopants to a two-dimensional layer with a thickness comparable to the domain wall, i.e. of the
order of a few unit cell widths.

There are a number of reasons why diffusion in a domain wall may be different from that
in the bulk [5].

(1) *The domain wall structure may be more or less dense than that in the domain wall.*
Consider for example two twin domains with strain tensors ϵ_+ and ϵ_-. Possible orientations of the twin wall may be calculated using the equation $x^{\mathrm{T}}(\epsilon_+ - \epsilon_-)x = 0$, where x is the vector (x, y, z). The equation describes the coordinates of planes parallel to the twin walls. The same equation may also be used to make deductions about the behaviour of the strain tensor within the domain wall, in particular which components of the strain tensor remain fixed within the wall and which are free to vary. The form of the equation which must be used is $x^{\mathrm{T}}(\epsilon_+ - \epsilon)x = 0$, where now x is a general vector in the plane of the domain wall; for instance if we take the domain wall as the $x = 0$ plane then $x = (0, y, z)$. ϵ is the strain tensor in the wall. In the case where plane is the $x = 0$ plane then the above equation forces ϵ_{22}, ϵ_{33} and ϵ_{23} to remain constant across the domain wall, but places no conditions on ϵ_{11}, ϵ_{12} and ϵ_{13}. If ϵ_{12} is the order parameter of the phase transition, ϵ_{11} describes a dilatational strain perpendicular to the wall which can either open up the wall structure or cause it to become more dense: the value of ϵ_{11} in the wall has a large impact on the diffusion in the wall [5]. ϵ_{13} describes a shear strain in a different sense from that of the order parameter. Again a shear within the wall would have a large effect on the diffusion tensor within the wall. In principle these strains within the wall could be detected by x-ray diffraction; in practice the resolution of the technique is too low to allow the strains within the wall to be determined.

(2) *The atoms in the domain wall may be less strongly held in place than those in the bulk.*
A displacive phase transition must be due to a multiple well potential in the interatomic interaction parameters. In the domains of the material the atoms will lie in one or the other of the wells of the potential. However, in the domain walls, the atoms may lie on the hills of the potential. The contribution an interatomic potential makes to the potential well in which the atom sits depends on the curvature of the potential. In the bulk the positive curvature of the potential well will lead to the atom being held more strongly in place. In the domain wall the negative curvature of the potential hill will lead to the atom being less strongly held in place. Therefore we expect the atoms in a domain wall to be held less strongly in place than in the bulk. An atom moving through the crystal will have to push other atoms aside in order to move from local minimum to local minimum, and the energy needed to do this will be reduced if the atoms are held in place less strongly. To illustrate this consider a system in which the order parameter is some linear combination of strains ϵ. The simplest possible Landau free energy describing this system is

$$G = -\frac{a}{2}\epsilon^2 + \frac{b}{4}\epsilon^4 + \frac{g}{2}\left(\frac{\partial\epsilon}{\partial z}\right)^2. \tag{1}$$

The domain wall profile is $\epsilon = \epsilon_0 \tanh(\frac{z}{w})$ where $\epsilon_0 = \sqrt{\frac{a}{b}}$ and $w = \sqrt{\frac{2c}{a}}$. The elastic constant associated with ϵ is given by $C = \frac{\partial^2 G}{\partial\epsilon^2} = -a + 3bQ^2$. The variation of C across the wall is

$$C = a\left[3\tanh\left(\frac{z}{w}\right) - 1\right]. \tag{2}$$

The elastic constant is reduced and in fact becomes negative within the wall.

(3) *The domain wall may be charged.* In a ferroelectric material the polarization may vary across a domain wall. In this case the charge density within the wall will be given by the divergence of the polarization vector, i.e. $\rho = \nabla \cdot P$. If n is the normal to the domain wall then the equation may be rewritten as $\rho = \partial_n P_n$. The polarization is likely
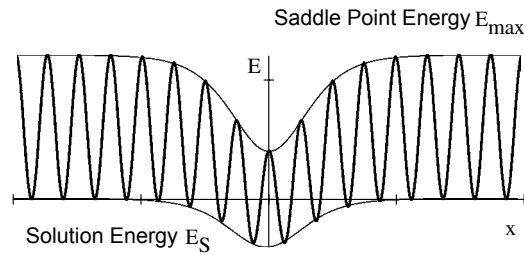
Saddle Point Energy E_{max}

Solution Energy E_S

Figure 1. This figure shows how three important energies, the solution energy E_S, the saddle point energy E_{max}, and the hopping energy E_H, may be expected to vary across a domain wall. The solution energy and the saddle point energy are shown explicitly on the graph, the hopping energy E_H is given by the difference between them $E_H = E_{max} - E_S$. The hopping energy is the potential barrier the atom must surmount in order to move from one site to another.

to have a hyperbolic tangent behaviour across the domain wall (or no variation at all): $P_n = P_0 \tanh(\frac{z}{w})$, in which case the charge density across the wall will be given by

$$\rho = \frac{P_0}{w}\left[1 - \tanh\left(\frac{z}{w}\right)^2\right].$$ (3)

(4) *The domain wall may contain a higher number of vacancies than the bulk.* Since the domain wall will have a different structure and different local elastic constants from the bulk, the energy of formation of a vacancy E_V will be different. Since the vacancy concentration is given by $c = \exp(-\frac{E_V}{k_B T})$, it will vary with position relative to the domain wall. A change in the concentration of vacancies will have a profound effect on interstitial diffusion as well as strongly affecting the diffusion of substitutional impurities.

Given that the properties of a domain wall may be quite different from those of the bulk we now need to consider how the standard diffusion equation will be modified. In a homogeneous material the form of Fick's first law that describes how an atomic flux J is related to the gradient of the concentration c by the diffusion constant D is $J = -D\nabla c$. In a system with domain walls Fick's first law is modified from this form. In such a system the solution energy E_S of an atom within the domain wall will be different to the solution energy of an atom in the bulk. Therefore, in equilibrium the atomic concentration in the bulk and in the domain wall will be different, as predicted by the Boltzmann distribution. Fick's first law must therefore contain a term which describes the tendency of atoms to move into areas of low solution energy. The form of Fick's first law appropriate for this situation is

$$J = -D\nabla c - c\mu\nabla E_S$$ (4)

where μ is the mobility of the atoms. Both D and μ are functions of position relative to the domain wall, since both have an Arrhenius dependence on the hopping energy E_H, which is different in the domain wall and the bulk. Figure 1 shows how the hopping and solution energies may be expected to vary across a domain wall. D and μ are not independent, but are related by the Einstein relation, which follows from the condition that when the concentration is given by the Boltzmann distribution the net flux must be zero. The Einstein relation is $D = k_B T \mu$.

The second important equation in describing diffusion is Fick's second law. It is obtained by applying the equation describing the conservation of mass $\frac{\partial c}{\partial t} = -\nabla J$ to Fick's first law. In the case of a homogeneous material the diffusion equation is

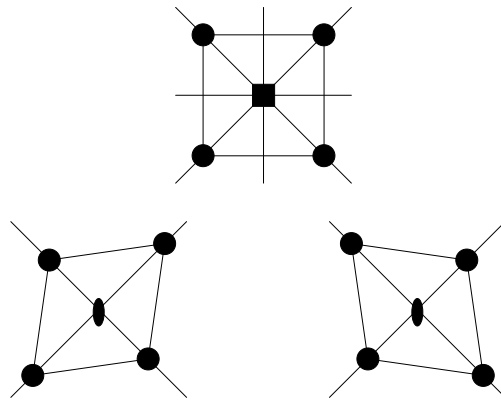$$\frac{\partial c}{\partial t} = D\nabla^2 c.$$ (5)

Figure 2. In the model used in the text the transition is from tetragonal $4/mmm$ symmetry to orthorhombic mmm symmetry. The above figure shows the symmetry change at the transition. Mirror planes and rotation axes perpendicular to the plane of the diagram are shown. There are two possible transition twins related by a reflection or a 90° rotation.
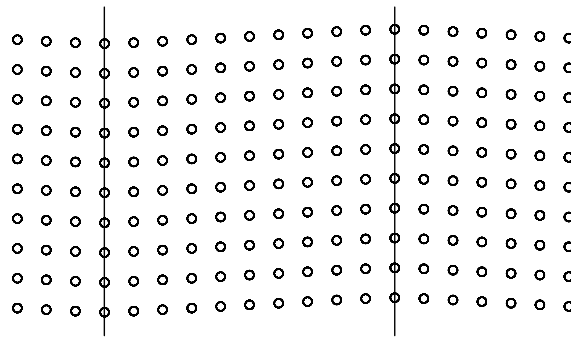

Figure 3. This diagram shows the system configuration as seen looking down the c-axis. The a-axis is horizontal and the b-axis is vertical. There are two domain walls, indicated by lines.

In a material with a domain wall microstructure the diffusion equation is given by

$$\frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c) + \nabla \cdot (c\boldsymbol{\mu}\nabla E_S). \tag{6}$$

Therefore, interstitial diffusion in a domain wall microstructure can be described by a hopping energy E_H and a solution energy E_S, which determine the form of the relevant diffusion equations. The functional forms of these energies depend on the properties of the domain wall, i.e. the structure of the domain wall, the local elastic constants, the charge of the domain wall and the vacancy concentration within the domain wall.

To investigate this in more detail we looked at the simplest possible model which displayed a domain microstructure and was capable of supporting diffusion. This is a three-dimensional ferroelastic lattice, similar to that studied in two dimensions by Novak and Salje [7, 8]. In its high-temperature form the lattice is tetragonal with an 'accidental' degeneracy of the lattice parameters setting $a = b = c$. The low-temperature form suffers an orthorhombic distortion in the form of an ϵ_{12} shear of the unit cell. Two different forms of the low-temperature unit cell are possible, described by opposite signs of ϵ_{12}, and thus domain walls are possible. The model is described in more detail in section 2. An interstitial atom, interacting with the lattice
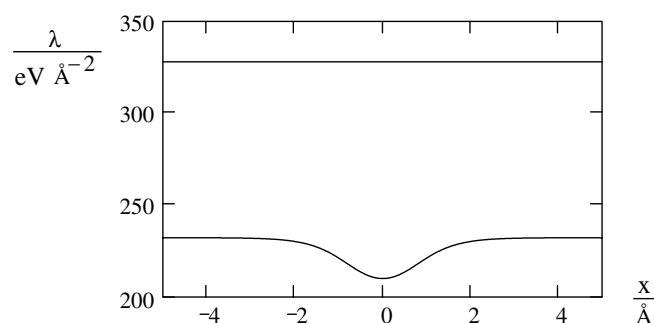
Figure 4. This graph shows the Einstein model prediction of the curvature of the potential well in which the lattice atoms move as a function of distance from the domain wall. The upper, flat trace shows λ_3, which is unaffected by the domain wall. The lower trace shows $\lambda_1 = \lambda_2$ which are reduced in the wall, indicating that lattice atoms are less strongly bound within the domain wall.
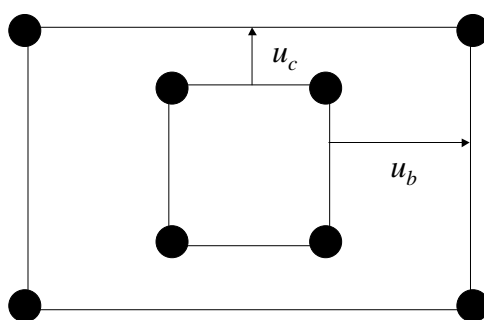

Figure 5. When the interstitial atom is at the saddle point it pushes it is nearest neighbours apart. The distance moved by these atoms parallel to the b-axis is u_b, the distance moved parallel to the c-axis is u_c.

atoms by a repulsive Lennard-Jones potential is introduced. In previous publications we used this model to investigate the diffusion of an solute atom in the limit of weak interaction with the lattice [5] and the surface structure of the domain wall [6].

In this work we describe the effect of increasing the interaction strength so that the interstitial atom does have a significant effect of the local structure of the lattice. Our aim in doing this is not simply to describe diffusion in our model but to evaluate approximations which may be applicable to real crystals. We investigate the case of diffusion perpendicular to the domain wall and calculate the saddle point energy. In the case when the interaction between the solute atom and the lattice atoms is weak the saddle point energy should be independent of position. Our results show clearly an elastic softening of the domain wall, i.e. we demonstrate a reduction in the saddle point energy which can only be explained by the atoms in the domain wall being less strongly held in place than the bulk atoms.

2. The model

To investigate the role of domain wall softening in diffusion we used a three-dimensional variant of the two-dimensional model used by Novak and Salje [7, 8] to investigate microstructure in ferroelastic materials. The model consists of a ferroelastic lattice with space group $P4/mmm$ in its high-temperature phase. The interactions within the model are chosen so that the high-
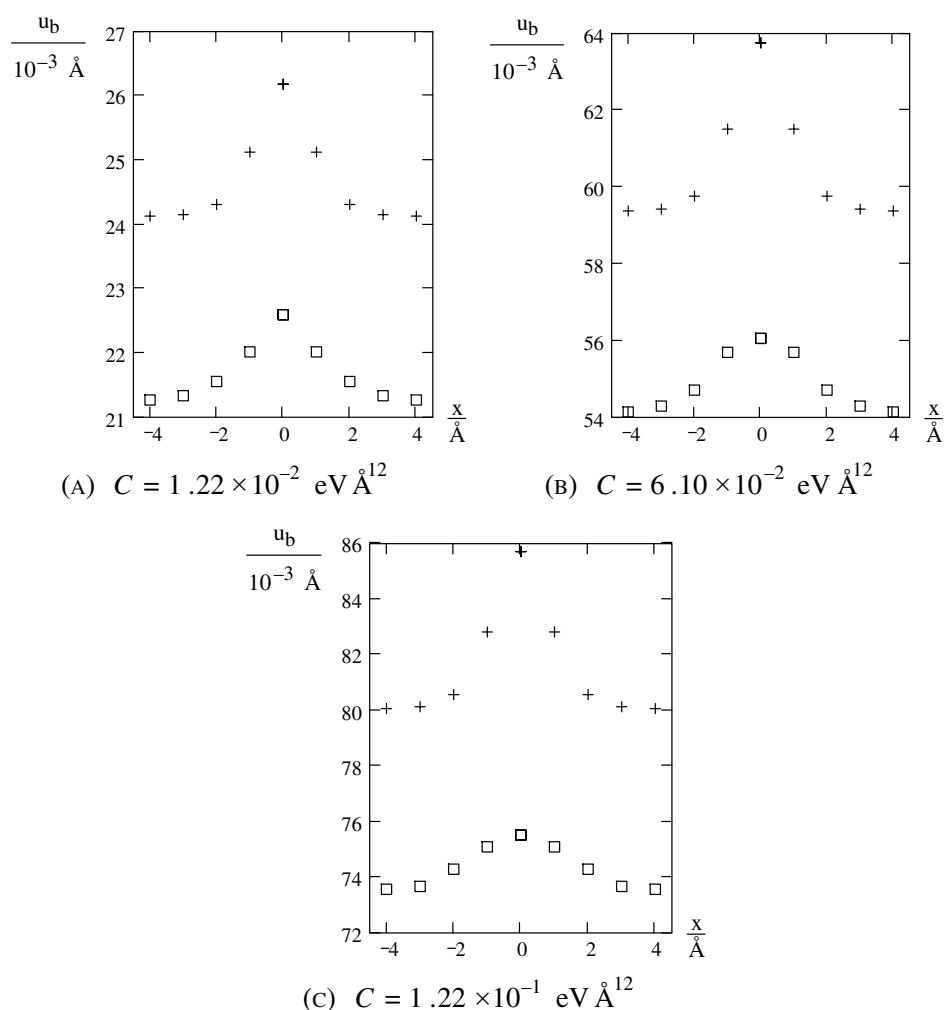
Figure 6. Displacements in the *b* direction at the saddle point. Open squares show numbers calculated from the numerical simulations and plusses are calculations from the Einstein model.

temperature phase is unstable with respect to an ϵ_{12} shear distortion. The space group of the low-symmetry form is *Pmmm* and two possible variants exist, as illustrated in figure 2. The atomic structure of the model is shown in figure 3. We investigate diffusion perpendicular to a domain wall in such a lattice, and show that the saddle point energy of the diffusing atom is significantly reduced in the domain wall. This is significant because the strain compatibility relation shows that neither dilatational nor shear strains may occur parallel to the domain wall in the absence of interactions with the solute atom. Therefore this reduction in the saddle point energy cannot be attributed to a change in the size or shape of the aperture through which the atom must pass at the saddle point. Instead an elastic softening of the lattice is indicated.

The functional forms of the interactions in the model are given in table 3. Each of the parameters of the potentials is given an interpretation in table 2 although this particular interpretation is not unique (for instance the roles of q_2 and q_4 could be exchanged). The parameters a_1 and q_2 are chosen to set the lattice parameter to 1 Å and the shear angle to θ_0.

(A) $C = 1.22 \times 10^{-2}$ eV $\mathring{A}^{12}$

(B) $C = 6.10 \times 10^{-2}$ eV $\mathring{A}^{12}$

(C) $C = 1.22 \times 10^{-1}$ eV $\mathring{A}^{12}$
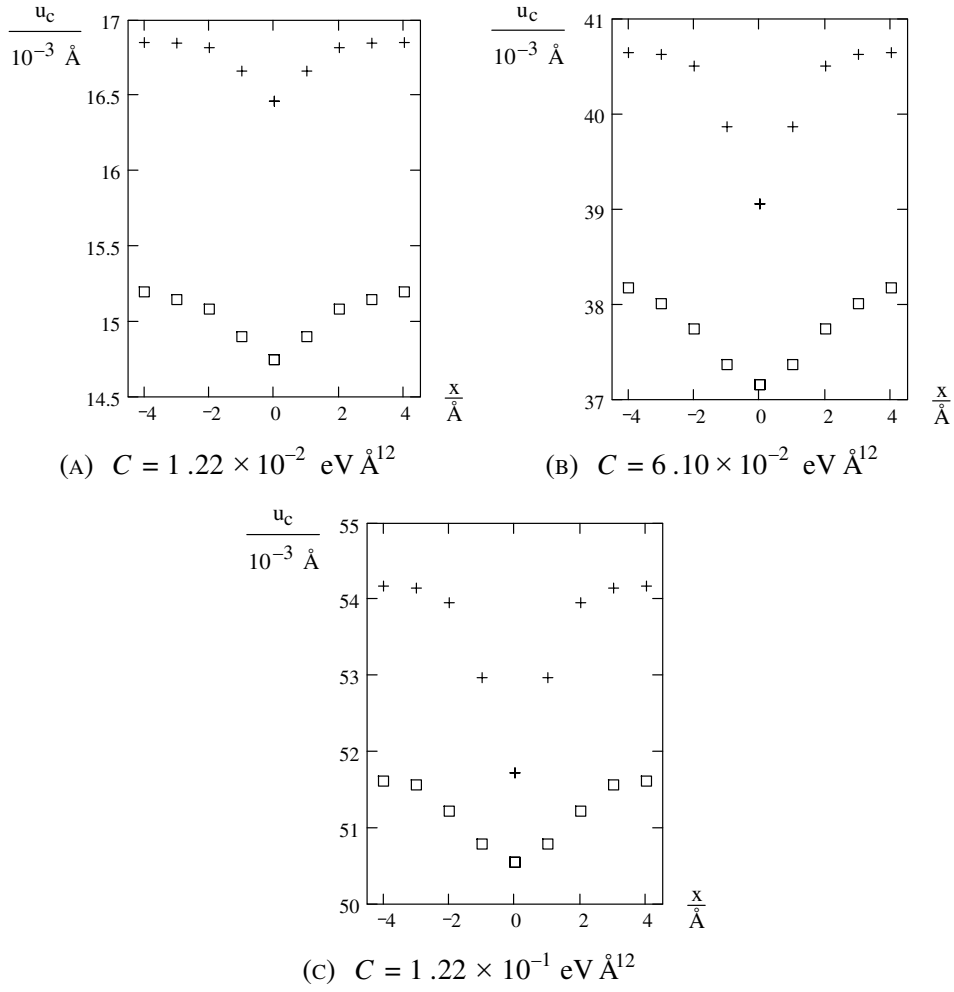
Figure 7. Displacements in the c direction at the saddle point. Open squares show numbers calculated from the numerical simulations and plusses are calculations from the Einstein model.

For this to be the case we must have

$$a_1 = -\frac{2k_3a_3}{k_1} + \frac{\sqrt{2}}{2}\frac{q_3\theta_0}{k_1} \tag{7}$$

$$q_2 = -\frac{q_4}{2} + \frac{\sqrt{2}}{2}q_3\theta_0. \tag{8}$$

The domain wall structure in such a model can be described by two strains, the shear strain ϵ_{xy} and the dilatational strain perpendicular to the wall ϵ_{xx}. The free energy of the system in terms of these strains is given by

$$F[\epsilon_{xx}, \epsilon_{xy}] = \int \left\{ \frac{\sqrt{2}}{2}q_3\theta_0\epsilon_{xx} + \left(k_1 + 2k_3 - \frac{q_4}{4}\right)\epsilon_{xx}^2 - \frac{q_4}{4}\epsilon_{xy}^2 \right.$$

$$\left. + \frac{q_4}{8\theta_0^2}\epsilon_{xy}^4 + \frac{\sqrt{2}}{2}\frac{q_3}{\theta_0}\epsilon_{xy}^2\epsilon_{xx} + \frac{k_3a_3}{4}\left(\frac{\partial\epsilon_{xy}}{\partial x}\right) \right\} dx. \tag{9}$$

$$\text{(A)} \quad C = 1.22 \times 10^{-2} \text{ eV Å}^{12}$$

$$\text{(B)} \quad C = 6.10 \times 10^{-2} \text{ eV Å}^{12}$$

$$\text{(C)} \quad C = 1.22 \times 10^{-1} \text{ eV Å}^{12}$$

Figure 8. Saddle point energies. Open squares show numbers calculated from the numerical simulations and plusses are calculations from the Einstein model.

This free energy can be minimized to give the structure of the domain wall. The shear angle profile across the domain wall is given by

$$\epsilon_{xy} = \theta_0 \tanh\left(\frac{x}{w}\right). \tag{10}$$

The dilatational strain across the wall is given by

$$\epsilon_{xx} = \frac{q_3 \theta_0 \sqrt{2}}{4k_1 + 8k_3 - q_4}\left[1 - \tanh^2\left(\frac{x}{w}\right)\right]. \tag{11}$$

(A) $C = 1.22 \times 10^{-2}$ eV Å^{12}

(B) $C = 6.10 \times 10^{-2}$ eV Å^{12}
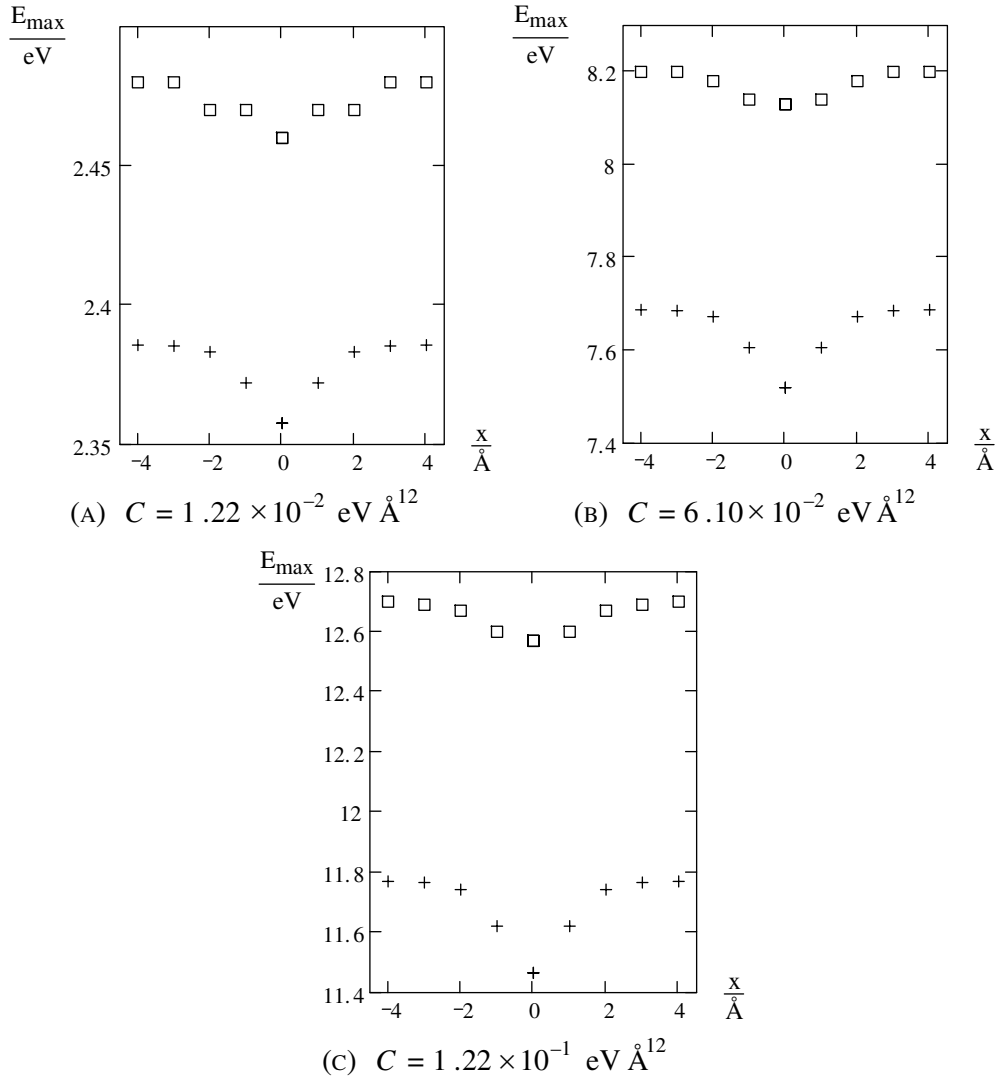
(C) $C = 1.22 \times 10^{-1}$ eV Å^{12}
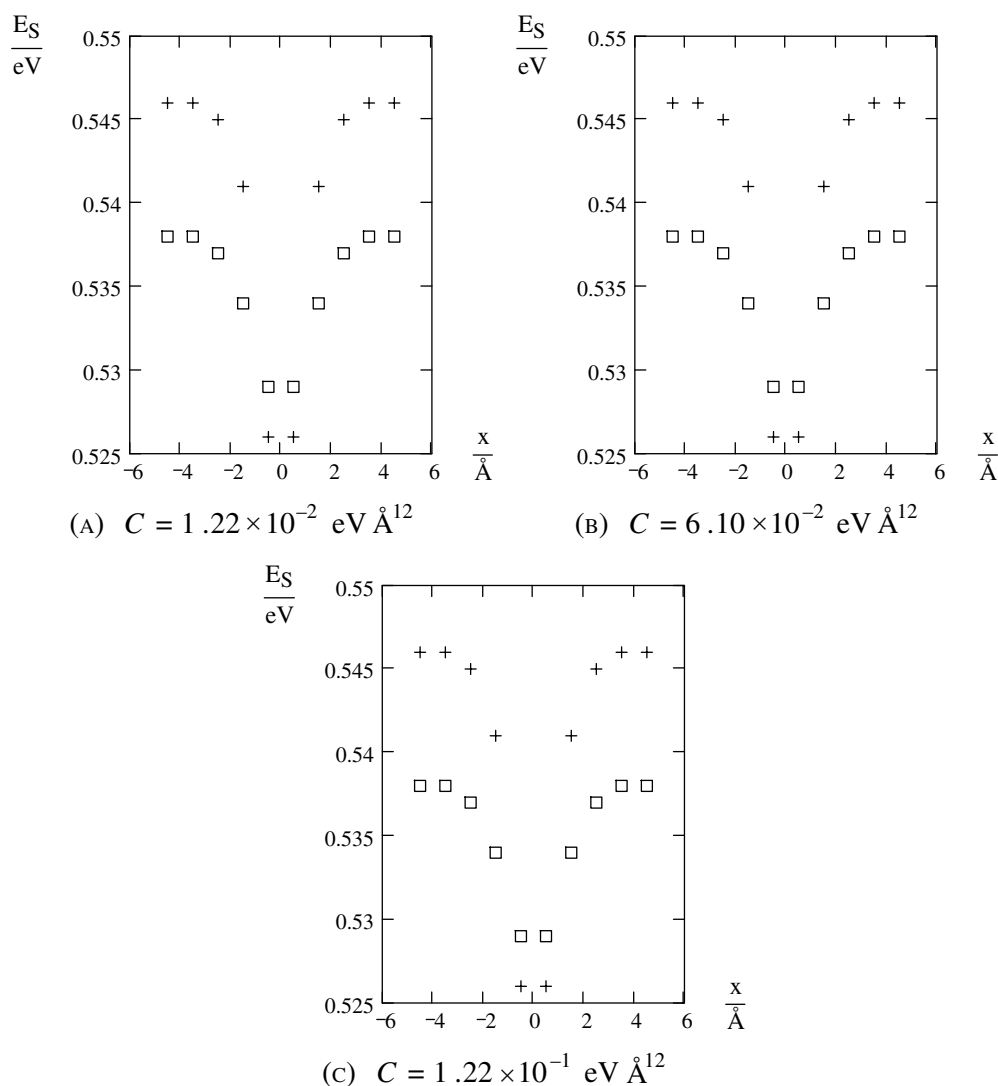
Figure 9. Solution energies. Open squares show numbers calculated from the numerical simulations and plusses are calculations from the Einstein model.

The domain wall width is given by

$$w = \sqrt{\frac{2k_3 a_3 (4k_1 + 8k_3 - q_4)}{q_4(4k_1 + 8k_3 - q_4) - 4q_3^2}}. \tag{12}$$

The parameters of the potentials are chosen so that the domain wall width $w = 1$ Å, and the dilatational strain $\epsilon_{xx} = 0$. The model was implemented numerically using the molecular dynamics code DL_POLY [10] running at zero temperature.

We can attempt to calculate the diffusion constants of the system using simple models. The simplest model is to assume that the diffusing atom does not perturb the structure of the crystal as it travels through. The results of calculations using this approximation are described in [5]. The second level of approximation is to take some account of the distortion of the crystal

Table 1. Numerical values of parameters in the model.

Parameter	Value
k_1 (eV Å^{-2})	50.0
k_3 (eV Å^{-2})	−0.665
q_2 (eV Å^{-2})	−2.5
q_3 (eV Å^{-3})	0.0
q_4 (eV Å^{-4})	7.23
a_1 (Å)	0.816
a_3 (Å)	−6.92
θ_0 (deg)	4.3

Table 2. Interpretation of the terms in the model.

Parameter	Interpretation
k_1	Used to adjust the C_{xxxx} elastic constant (table 4)
k_3	Used to adjust the gradient term associated with ϵ_{xx} (equation (9))
q_2	Used to set the shear angle to θ_0 see equation (8)
q_3	Used to adjust the value of ϵ_{xx} within the domain wall (equation (9))
q_4	Used to adjust the C_{xyxy} elastic constant (table 4)
a_1	Used to set the lattice parameters a and b to 1 Å
a_3	Used to adjust the gradient term associated with ϵ_{xy} (equation (9))

Table 3. Table showing the interaction potentials. The symbol $\langle UVW \rangle$ refers to directions related by tetragonal symmetry to the $[UVW]$ direction.

Potential	Interacting atoms	Functional form
f_1	$\langle 100 \rangle$	$\dfrac{k_1}{2}(r - a_1 - 1)^2$
f_2	$\langle 110 \rangle$	$\dfrac{q_2}{2}(r - \sqrt{2})^2 + \dfrac{q_3}{3\theta_0}(r - \sqrt{2})^3 + \dfrac{q_4}{4\theta_0^2}(r - \sqrt{2})^4$
f_3	$\langle 200 \rangle$	$\dfrac{k_3}{2}(r - a_3 - 2)^2$
f_4	$\langle 001 \rangle$	$\dfrac{k_1}{2}(r - 1)^2$
f_5	$\langle 101 \rangle$	$\dfrac{k_1}{2}(r - \sqrt{2})^2$

Table 4. Elastic constants of the system given in terms of the parameters of the potentials. The units of the elastic constants are atomic, i.e. eV Å^{-3}.

Modulus	Value
C_{xxxx}	$2k_1 + 4k_3 + q_4$
C_{zzzz}	$3k_1$
C_{xxyy}	q_4
C_{xxzz}	k_1
C_{xyxy}	q_4
C_{xxxy}	$q_3\sqrt{2}$

structure by the diffusing atom. The simplest model in which this effect can be included is the Einstein model. This model is a mean field model of the atomic interactions and assumes that each atom moves in an anisotropic harmonic potential well due to its interaction with

its neighbours (assumed to be static). Surprisingly even such a simple model as this gives qualitatively correct results for the atomic displacements and the saddle point energy. The potential energy may be written, in the Einstein model approximation, as

$$V = \frac{\lambda_1}{2}u_1^2 + \frac{\lambda_2}{2}u_2^2 + \frac{\lambda_3}{2}u_3^2. \tag{13}$$

The principal axes 1, 2 and 3 are in the [110], [1$\bar{1}$0] and [001] directions. The values of λ depend on the local value of the shear angle and its spatial gradient:

$$\lambda_1 = 4k_1 + 2k_3 + 3k_3a_3 - q_4 + 3q_4\left(\frac{\theta}{\theta_0}\right)^2 + \frac{3}{4}q_4\left(\frac{\partial_z\theta}{\theta_0}\right)^2 + 2\sqrt{2}q_3\frac{\theta}{\theta_0} \tag{14}$$

$$\lambda_2 = 4k_1 + 2k_3 + 3k_3a_3 - q_4 + 3q_4\left(\frac{\theta}{\theta_0}\right)^2 + \frac{3}{4}q_4\left(\frac{\partial_z\theta}{\theta_0}\right)^2 - 2\sqrt{2}q_3\frac{\theta}{\theta_0} \tag{15}$$

$$\lambda_3 = 6(k_1 + k_3a_3). \tag{16}$$

In the case of the potential set used in this work $\lambda_1 = \lambda_2$ because $q_3 = 0$. Figure 4 shows the values of $\lambda_1 = \lambda_2$ and λ_3 across the domain wall. The graph shows that although λ_3 is completely unaffected by the domain wall, $\lambda_1 = \lambda_2$ shows a 10% drop within the wall. This suggests that lattice atoms are less strongly bound within the wall.

3. Results

In the previous section we described a model ferroelastic lattice and calculated the strength of the interactions holding the atoms in their equilibrium positions within the framework of the Einstein approximation. In this section we compare the predictions of the Einstein model with the results of simulations with the aim of evaluating the usefulness of the Einstein approximation as a tool for discussing diffusion in real materials.

The quantity we chose to measure was the saddle point energy for diffusion in the [100] direction. The reason for this choice is that the size and shape of the aperture through which the atom must move is, in the absence of interactions with the solute atom, constrained by the strain compatibility condition to be a square of edge length 1 Å with lattice atoms at each vertex. Any variations in this saddle point energy must be due to changes in the wall elasticity rather than to structural changes.

As well as measuring the saddle point energy E_{max} we also calculated the displacements of the lattice atoms from their equilibrium positions as shown in figure 5 and the solution energies E_S. Values of the quantities u_b, u_c and E_{max} were calculated by simulation, by holding the solute atom fixed at the centre of the aperture and allowing the system to relax. (The zero of energy is taken as the energy of the relaxed lattice in the absence of the solute atom.) E_S was calculated by placing the atom in the centre of a distorted cubic interstice and allowing the system to relax. The theoretical values were calculated by relaxing the nearest neighbours to the solute atom using the Einstein model potential energies. We calculated the aforementioned quantities for distances of 0–4 Å from the domain wall centre and for values of the interaction parameter C of 1.22×10^{-2}, 6.10×10^{-2} and 1.22×10^{-1} eV Å^{12}. The results are shown in figures 6–9. Comparisons of the values obtained for the bulk and the wall are shown in tables 5 and 6.

4. Discussion

Considering the simplicity of the model used to fit the simulation data the model is remarkably successful. It predicts bulk quantities to within about 10%. The difference between bulk

Table 5. Comparison of atomic displacements calculated numerically with those predicted by the Einstein model. The atomic displacements are calculated for the case where the solute atom is at the position of the saddle point. 'Difference' refers to the difference between the bulk value and the wall value. The values for the bulk show an error of about 10%. The predictions made for the difference between the bulk value and the wall value are the correct order of magnitude, but may differ by as much as a factor of 2.

Interaction parameter, C	Simulation	Model	Error (%)
Displacement in the [010] direction (Å)			
Bulk			
1.22×10^{-2}	2.13×10^{-2}	2.41×10^{-2}	13
6.10×10^{-2}	5.41×10^{-2}	5.94×10^{-2}	10
1.22×10^{-1}	7.36×10^{-2}	8.01×10^{-2}	9
Difference			
1.22×10^{-2}	1.32×10^{-3}	2.05×10^{-3}	52
6.10×10^{-2}	1.92×10^{-3}	4.38×10^{-3}	129
1.22×10^{-1}	1.95×10^{-3}	5.64×10^{-3}	189
Displacement in the [001] direction (Å)			
Bulk			
1.22×10^{-2}	1.52×10^{-2}	1.69×10^{-2}	11
6.10×10^{-2}	3.82×10^{-2}	4.06×10^{-2}	6
1.22×10^{-1}	5.16×10^{-2}	5.24×10^{-2}	5
Difference			
1.22×10^{-2}	4.50×10^{-4}	3.89×10^{-4}	13
6.10×10^{-2}	1.02×10^{-3}	1.59×10^{-3}	57
1.22×10^{-2}	1.07×10^{-3}	2.45×10^{-3}	130

and wall quantities are predicted less accurately but the model gets the order of magnitude correct and predicts the correct trends with distance from the domain wall and with increasing interaction parameter.

These results clearly show that even in a topologically perfect crystal, the difference between a domain wall and the bulk material is not purely structural. The domain wall is softer than the bulk material, which means that diffusion in a domain wall will be faster than predictions based solely on structural considerations would predict. The reason for the domain wall softening can easily be seen within the Einstein model approximation. The interaction responsible for the softening of λ_1 and λ_2 is f_2 (see table 3). This is a double-well potential which acts across the [110][1$\bar{1}$0] unit cell diagonals. In the bulk state of the system the lengths of these diagonals are such that the interatomic distances along the diagonals fall in the two minima of the potential. Thus f_2 makes a positive contribution to λ_1 and λ_2. In the wall the lengths of the diagonals are the same and fall on the maximum between the two potential wells. Therefore, in the wall f_2 makes a negative contribution to λ_1 and λ_2. Similar arguments would apply if the double-well potential was a three-body potential rather than a pair potential. The other potentials all have single minima and thus their contribution to the λs do not change

5. Conclusions

Domain wall diffusion is a process that may prove of great technical importance, allowing fine spatial control of doping within materials. To fully exploit the potential of this, a good

Table 6. Comparison of saddle point, solution, and hopping energies calculated numerically with those predicted by the Einstein model. 'Difference' refers to the difference between the bulk value and the wall value. The values for the bulk show an error of about 5%. The predictions made for the difference between the bulk value and the wall value are the correct order of magnitude, but may differ by as much as a factor of 2.5.

Interaction parameter, C	Simulation	Model	Error (%)
Saddle point energy (eV)			
Bulk			
1.22×10^{-2}	2.48	2.39	4
6.10×10^{-2}	8.20	7.69	6
1.22×10^{-1}	12.70	11.77	7
Difference			
1.22×10^{-2}	0.02	0.03	40
6.10×10^{-2}	0.07	0.17	140
1.22×10^{-1}	0.13	0.30	134
Solution energy (eV)			
Bulk			
1.22×10^{-2}	0.54	0.55	1
6.10×10^{-2}	2.32	2.34	1
1.22×10^{-1}	4.08	4.11	1
Difference			
1.22×10^{-2}	0.01	0.02	122
6.10×10^{-2}	0.03	0.08	186
1.22×10^{-1}	0.04	0.15	240
Hopping energy (eV)			
Bulk			
1.22×10^{-2}	1.94	1.84	5
6.10×10^{-2}	5.88	5.35	9
1.22×10^{-1}	8.62	7.66	11
Difference			
1.22×10^{-2}	0.01	0.01	27
6.10×10^{-2}	0.04	0.08	105
1.22×10^{-1}	0.09	0.16	82

understanding of the factors controlling diffusion within domain walls is needed. We have shown that a domain wall is elastically softer than the bulk phases of a material. This effect will (in the absence of competing effects, e.g. structural changes) tend to reduce the hopping energy in the wall and increase the wall diffusion rate.

References

[1] Aird A and Salje E K H 1998 Sheet superconductivity in twin walls: experimental evidence of WO$_{3-x}$ *J. Phys.: Condens. Matter* **10** L377–80
[2] Aird A and Salje E K H 2000 Enhanced reactivity of domain walls in WO$_3$ with sodium *Eur. Phys. J.* B **15** 205–10
[3] Bartels M, Hagen V, Burianek M, Getzlaff M and Bismayer U 2002 Impurity-induced resistivity of ferroelastic domain walls in doped lead phosphate *J. Phys.: Condens. Matter* **15** 957

[4] Calleja M, Dove M T and Salje E K H 2001 Anisotropic diffusion in twinned quartz: the effect of twin boundaries *J. Phys.: Condens. Matter* **13** 9445–54

[5] Lee W T, Salje E K H and Bismayer U 2002 Structure and transport properties of ferroelastic domain walls in a simple model *Phase Transit.* **76** 81

[6] Lee W T, Salje E K H and Bismayer U 2002 Surface structure of domain walls in a system with a domain wall pressure *J. Phys.: Condens. Matter* **14** 7091–910

[7] Novak J and Salje E K H 1998 Simulated mesoscopic structures of a domain wall in a ferroelastic lattice *Eur. Phys. J.* B **4** 279–84

[8] Novak J and Salje E K H 1998 Surface structure of domain walls *J. Phys.: Condens. Matter* **10** L359–66

[9] Salje E K H, Aird A, Locherer K, Hayward S, Novak J and Chrosch J 1999 Ferroelastic twin walls for nanotechnological applications *Ferroelectrics* **223** 1–10

[10] Smith W and Forester T R 1996 DL_POLY_2.0: a general-purpose parallel molecular dynamics simulation package *J. Mol. Graph.* **14** 136–41