Twin wall of cubic-tetragonal ferroelastics

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We derive solutions for the twin wall linking two tetragonal variants of the cubic-tetragonal ferroelastic transformation, including for the first time the dilatational and shear energies and strains. Our solutions satisfy the compatibility relations exactly and are obtained at all temperatures. They require four non-vanishing strains except at the Barsch-Krumhansl temperature $T_{BK}$ (where only the two deviatoric strains are needed). Between the critical temperature and $T_{BK}$, material in the wall region is dilated, while below $T_{BK}$ it is compressed. In agreement with experiment and more general theory, the twin wall lies in a cubic 110-type plane. We obtain the wall energy numerically as a function of temperature and we derive a simple estimate which agrees well with these values.

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Ferroelastic transformations are diffusionless, first-order, shape-changing phase changes in the solid state. In cubic-tetragonal (C-T) systems like Nb$_3$Sn, V$_3$Si, In-Tl alloys, Fe-Pd alloys and Ni$_2$MnGa, the cubic unit cell elongates (or contracts) along one of three axes to form a tetragonal unit cell; below the transition temperature $T_c$ there are three possible homogeneous products (variants) differing only in orientation.

Barsch and Krumhansl (BK) obtained an analytical solution for the twin wall linking two tetragonal variants of C-T ferroelastics. The dilatational and shear strains vanish identically, and the two remaining strains are functions of a single coordinate. The wall lies in a cubic 110-type plane, in agreement with experiment and as already known on more general grounds.

The BK solution is valid, however, at only a single temperature ($T = T_{BK}$). At any other $T$, the dilatational and shear strains are not zero, and the only known method to find the C-T twin wall structure requires solving the full three-dimensional (3D) partial differential equations (previous attempts at a 1D solution omitted the non-deviatoric strains). Some numerical solutions of these equations have been obtained, but no results have been given for the wall structure.

That is, 16 years after BK, the wall structure is still unknown except at $T_{BK}$.

The following solves this long-standing problem, which is of considerable physical interest, given the large strains and large magnetic-field effects in Ni$_2$MnGa. Specifically, we present a 1D solution for the C-T twin wall at all $T$. Our solutions, which include dilatational and shear energies and strains, satisfy the compatibility relations by virtue of analytical relations that we derive between the strains; these relations allow us to reduce the problem to the solution of ordinary, rather than partial, differential equations. We recover the BK solution at $T_{BK}$ and we present results at both higher and lower $T$.

The three paragraphs immediately following define the strains and the two parts of the free-energy density. The next two paragraphs obtain the key new results of our analysis, namely two relations between the strains, and the resulting Euler-Lagrange equations. The remaining paragraphs discuss the results from solution of these equations. We find that the twin-wall region is dilated near $T_c$ and compressed below $T_{BK}$.

Six strains are required to describe C-T ferroelastics, the dilatational strain $e_1$, the deviatoric strains $e_2$ and $e_3$, and the shear strains $e_4$, $e_5$ and $e_6$. With the coordinate axes along the four-fold axes, and in the small-strain approximation, these are

$$
e_1 = (u_{11} + u_{22} + u_{33})/\sqrt{3}, \quad e_2 = (u_{11} - u_{22})/\sqrt{2},$$
$$e_3 = (u_{11} + u_{22} - 2u_{33})/\sqrt{3}, \quad e_4 = (u_{11} + u_{22} + u_{33})/2$$

(1)

plus obvious expressions for $e_4$ and $e_5$. Here $u = (u_{11}, u_{22}, u_{33})$ is the displacement of the material point originally at $x$, and $u_{ij} = \partial_i u_i = \partial u_j/\partial x_j$. We need also the components $\omega_3 = (u_{12} - u_{21})/2$, etc. of the local rotation $\omega$.

The free energy $F$ is the integral $F = \int_V \mathcal{F} \, d^3 x$ of the free-energy density $\mathcal{F}$ over the undeformed volume $V$. For proper ferroelastics (where the strain is the primary order parameter), $\mathcal{F}$ is the sum of strain and strain-gradient parts. The strain part is

$$\mathcal{F}_s = \frac{A_1}{2} e_1^2 + \frac{A_2}{2} (e_2^2 + e_3^2) - \frac{B_2}{3} (e_3^3 - 3e_2^2 e_3)$$
$$+ \frac{C_2}{4} (e_2^2 + e_3^2)^2 + \frac{A_4}{2} (e_4^2 + e_5^2 + e_6^2).$$

(2)

In Voigt notation, the dilatational and shear constants are $A_1 = C_{111} + C_{112}$ and $A_4 = 4C_{44}$ respectively, with both $> 0$ for stability; the corresponding terms in the density were omitted in previous treatments. The coefficient $A_2$ depends on temperature as $A_2 = A_2'(T - T_0)$, where $T_0$ is the stability limit of the cubic phase and $A_2'$ is a material-dependent constant; above $T_c$, $A_2 = C_{111} - C_{112}$. For $A_2 > 4B_2'^2/C_2$, the energy has only the cubic minimum (all strains zero). For $A_2 < 4B_2'^2/C_2$, there are in addition three degenerate minima symmetrically located in the plane of the deviatoric strains:
\[ e_2 = 0 \]  
\[ e_2 = -\sqrt{3}e_{30}/2 \]  
\[ e_2 = \sqrt{3}e_{30}/2 \] \hspace{1cm} (3a) \hspace{1cm} (3b) \hspace{1cm} (3c)

with \( e_1 = e_4 = e_5 = e_6 = 0 \) and \( e_{30} = \left[ B_2 + (B_2^2 - 4A_2C_2)^{1/2} \right] / (2C_2) \); \hspace{1cm} (4)

The tetragonal four-fold axes are in the 3, 1 and 2 directions respectively. The C-T transition, which is first-order, occurs at \( A_2 = \frac{1}{4}B_2^2/C_2 \) where \( e_{30} = \frac{1}{4}B_2/C_2 \).

The free-energy density requires also strain-gradient terms, so that energy is required to introduce variant walls (otherwise the system can subdivide into arbitrarily fine variants). We keep only the two invariants quadratic in the deviatoric strain derivatives:

\[ F_{sg} = \frac{d_2}{2} \left[ (e_{21}^2 + (e_{22}^2) + (e_{23}^2) \right] + \frac{d_3}{2} \left[ (e_{31}^2 + (e_{32}^2) + (e_{33}^2) \right] \hspace{1cm} (5) \]

where \( e_{21}^2, e_{22}^2, e_{31}^2 \) and \( e_{32}^2 \) are obtained from \( e_2 \) and \( e_3 \) by \( 2\pi/3 \) rotations about the cubic 111 axis:

\[ e_{21}^2 = (u_{22} - u_{33})/\sqrt{2} = (-e_2 + \sqrt{3}e_3)/2 \],
\[ e_{22}^2 = (u_{33} - u_{11})/\sqrt{2} = (-e_2 - \sqrt{3}e_3)/2 \],
\[ e_{31}^2 = (u_{12} + u_{33} - 2u_{11})/\sqrt{6} = (-e_3 - \sqrt{3}e_2)/2 \],
\[ e_{32}^2 = (u_{33} + u_{11} - 2u_{22})/\sqrt{6} = (-e_3 + \sqrt{3}e_2)/2 \].

Both terms are transparently invariant and non-negative, and so we have the stability requirements \( d_2 \geq 0 \) and \( d_3 \geq 0 \) (which differ from those in Ref. 3); contact with previous treatments is made by writing \( d_2 = g_2 - g_3 \) and \( d_3 = g_2 + g_3 \), resulting in

\[ F_{sg} = \frac{1}{2}g_2[(\nabla e_2)^2 + (\nabla e_3)^2] + \frac{1}{2}g_3\left\{ \frac{1}{2}[(e_{21}^2 - (e_{31}^2)]^2 \right\} + \frac{1}{2}[(e_{22}^2 - (e_{32}^2)]^2 - [(e_{23}^2 - (e_{33}^2)]^2 \right\} \right. \]
\[ + \sqrt{3}(e_{21}e_{31} - e_{22}e_{32}) \}. \hspace{1cm} (7) \]

We seek the solution linking the variants with four-fold axes in the 1 and 2 directions, Eqs. (3b) and (3c); the results for this pair are simpler than for the others. The method is easily extended to treat a twin band. We assume a solution with \( e_4, e_5, \omega_1 \) and \( \omega_2 \) = 0 all identically zero, and with the other four strains (and \( \omega_3 \)) independent of \( x_3 \). The strains are not independent for physical settings like a twin wall where the strains depend on position; rather, they are linked by the compatibility relations (necessary and sufficient conditions that the strains be derivable from the displacement). The nine first-order relations, of the form \( u_{i,j,k} = u_{i,k,j} \), involve the first derivatives of the strains and the rotation components \( \omega_i \). The more familiar second-order relations, which involve the second derivatives of the strains, are easily obtained by differentiation to eliminate the \( \omega_i \). By virtue of the above assumptions, only the relations

\[ \partial_2 \left( \sqrt{2}e_1 + \sqrt{3}e_2 + e_3 \right) / \sqrt{2} = \partial_1 (e_6 + \omega_3) \right. \]
\[ \partial_1 (\sqrt{2}e_1 - \sqrt{3}e_2 + e_3) / \sqrt{6} = \partial_2 (e_6 - \omega_3) \right. \]
\[ \partial_1 (e_1 - \sqrt{2}e_3) = 0 \]
\[ \partial_2 (e_1 - \sqrt{2}e_3) = 0 \] \hspace{1cm} (8)

need be considered. We try for functions of \( X = x_1 \cos \beta + x_2 \sin \beta \) alone; a similar 1D solution is not possible for a cubic-tetragonal soliton. The compatibility relations are then

\[ \sin \beta \left( \sqrt{2}e_1 + \sqrt{3}e_2 + e_3 \right) / \sqrt{2} - \cos \beta (e_6 + \omega_3) = K_1 \]
\[ \cos \beta \left( \sqrt{2}e_1 - \sqrt{3}e_2 + e_3 \right) / \sqrt{6} - \sin \beta (e_6 - \omega_3) = K_2 \]
\[ e_1 - \sqrt{2}e_3 = K_3 \] \hspace{1cm} (9)

The constants \( K_1 \), \( K_2 \) and \( K_3 \) are evaluated from the boundary conditions at \( X = \pm \infty \), namely \( e_2 = \pm \frac{1}{\sqrt{2}}\sqrt{3}e_3 \), \( e_3 = -\frac{1}{\sqrt{2}}\sqrt{3}e_3 \), \( e_1 = e_6 = 0 \), and \( \omega_3 = \pm \Omega \). One finds easily that a solution is possible only if \( \cos 2\beta = 0 \), and so \( X = (x_1 \pm x_2)/\sqrt{2} \) that is, the walls lie in the 110 or 110 planes. In this way, we find the key new results relating \( e_1 \) and \( e_6 \) to the deviatoric strains:

\[ e_1(X) = \sqrt{2}e_3(X) + e_{30}/2 \]
\[ e_6(X) = \pm \sqrt{3}/2 e_3(X) + e_{30}/2 \] \hspace{1cm} (10)

plus \( \omega_3(X) = \pm e_2(X)/\sqrt{2} \). These results are independent of the details of the free-energy density (they apply whether or not the dilatational and shear energies appear in \( F \)).

Since the compatibility relations are satisfied, we can use the density

\[ F_{twin} = \frac{A_{ds}}{2} \left( e_3 + e_{30}/2 \right)^2 + \frac{A_2}{2} (e_2^2 + e_3^2) - \frac{B_2}{3} (e_3^2 - 3e_2^2) \]
\[ + \frac{C_2}{4} (e_2^2 + e_3^2)^2 + \frac{D_2}{2} \left( \frac{de_2}{dX} \right)^2 + \frac{D_3}{2} \left( \frac{de_3}{dX} \right)^2 \] \hspace{1cm} (11)

and minimize \( F \) with respect to \( e_2 \) and \( e_3 \). Here \( A_{ds} = 2A_1 + \frac{1}{4}A_4 \), \( D_2 = \frac{1}{4}d_2 + \frac{1}{4}d_3 \), and \( D_3 = \frac{1}{4}d_2 + \frac{1}{4}d_4 \); adding the diagonal invariants \( \frac{1}{2}d_1(\nabla e_1)^2 \) and \( \frac{1}{2}d_4(\nabla e_4)^2 + (\nabla e_5)^2 + (\nabla e_6)^2 \) (with \( d_1 \) and \( d_4 > 0 \)) to the density of Eq. (5) leaves \( D_2 \) unchanged while adding \( 2d_1 + \frac{1}{4}d_4 \) to \( D_4 \). The corresponding Euler-Lagrange equations are

\[ A_2e_2 + 2B_2e_2e_3 + C_2e_2(e_2^2 - e_3^2) = D_2d^2e_2/dX^2 \] \hspace{1cm} (12a)
\[ A_{ds}(e_3 + e_{30}/2) + A_2e_3 + B_2(e_2^2 - e_3^2) + C_2e_3(e_2^2 + e_3^2) = D_3d^2e_3/dX^2 \] \hspace{1cm} (12b)
The term $A_{ds}(e_3 + e_{30}/2)$ in Eq. (12), new with this article, results from satisfying the compatibility relations. The same equations are obtained, after integrations, on using the density of Eqs. (2) plus (3), demanding that $F$ be stationary with respect to the displacement, and only then using Eqs. (10). The boundary conditions are

$$e_2(\pm \infty) = \pm \sqrt{3}e_{30}/2, \quad e_3(\pm \infty) = -e_{30}/2. \quad (13)$$

At $A_2 = -2B_2^2/C_2$, which defines the temperature $T_{BK}$, the solutions are

$$e_2 = (\sqrt{3}e_{30}/2) \tanh(\kappa X), \quad e_3 = -e_{30}/2 \quad (14)$$

with $\kappa^2 = 3B_2^2/(2C_2D_2)$; the $A_{ds}$ term and the dilational and shear strains all vanish identically. We note that $T_{BK}$ may possibly be identified experimentally as the temperature where $e_{30} = 2B_2/C_2$ is three times the value at $T_c$.

At other temperatures, the strains $e_1$ and $e_0$ are not zero, and the equations must be solved numerically. We define the reduced temperature $\tau = (T - T_0)/(T_c - T_0)$; then $\tau = 1$ at the transition and $\tau = -9$ at $T = T_{BK}$. We also take $D_3 = D_2$.

To estimate the size of these effects, we use data for FePd alloys. The data quoted in Ref. 2 give $T_c = 268.6K$, $T_0 = 265K$ and $T_{BK} = 233K$. Combining these with data from Refs. 3 we find that $A_{ds}/A_2(T = T_c)$ has a lower limit of 200 based on the smallest observed values for $A_2$; we use a more conservative estimate of 400. Between $T_c$ and $T_{BK}$, the volume change $\Delta V/V$ at the centre of the wall reaches a maximum at $T \approx 258K$, with a very small value $\approx 10^{-4}$. At $T = 0$ we find $\Delta V/V \approx 10^{-2}$.

Figure 1 shows $e_2$ and $e_3$ as functions of position. The horizontal axis is scaled by $\kappa$ (see Eq. 14) defined at $T_{BK}$. The parameter $A_{ds}$ is $A_0(T_c - T_0)$; the temperatures $T = T_c$, $T = T_{BK}$ and $T < T_{BK}$ correspond to $\tau = 1$, $-9$ and $-50$ respectively.

Figure 1 shows $e_2$ and $e_3$ as functions of $X$ at three different temperatures, $T_c$ (which is $> T_{BK}$), $T_{BK}$ and $T < T_{BK}$, as determined from numerical solution of Eqs. (12) and (13). The value $A_{ds} = A_0(T_c - T_0) = A_2(T = T_c)$, which is rather soft, was chosen for display purposes; for larger values, $e_3$ remains close to $-e_{30}/2$. One sees that $e_3 + 1/2e_{30}$ is $> 0$ or $< 0$ for $T > T_{BK}$ or $< T_{BK}$ respectively. From Eqs. (10) then, the wall region is dilated near $T_c$ and compressed below $T_{BK}$.

FIG. 2. Trajectories in the $(e_3, e_2)$ plane for a twin wall linking two of the three tetragonal variants (solid circles). The parameter $A_{ds}$ and the temperatures are as in Figure 1.

Figure 2 shows twin-wall trajectories in the $(e_3, e_2)$ plane. The trajectories bow toward the third variant for $T_{BK} < T < T_c$, and away for $T < T_{BK}$. They shift toward the vertical for larger $A_{ds}$.

Reference 3 in effect, assumed that $A_1 = A_6 = 0$ and so the term $A_{ds}(e_3 + e_{30}/2)$ was absent from their differential equations. Solution of these equations, done only near $T_c$, gave trajectories which passed close to the origin. We point out however that the origin is not the cubic state but rather a highly dilated, highly sheared state with $e_1 = e_{30}/\sqrt{2}$ and $e_6 = \pm \sqrt{3/8}e_{30}$, as seen from Eqs. (10). Reference 3 which also assumed in effect that $A_1 = A_6 = 0$, proposed a trajectory that is a $2\pi/3$ circular arc centered at the origin. As evident from Figure 2, this is possibly useful only for $T \ll T_{BK}$.

The wall energy $W$ (per unit area) is the energy required to form an interface between two variants:

$$W = \int_{-\infty}^{\infty} (F_{twin} - F_h) \ dX \quad (15)$$

where $F_{twin}$ is the density (11) for the twin-wall solution of Eqs. (12) and (13), and
\[ F_h = \frac{1}{2} A_2 e_{30}^2 - \frac{1}{3} B_2 e_{30}^3 + \frac{1}{4} C_2 e_{30}^4 \]  

(16)

is the density for a single variant. Although not directly observable, \( W \) has physical content and so we provide the following.

![Diagram of numerical and variational wall energies as functions of the dimensionless temperature \( \tau \). The vertical axis is scaled by the wall energy at \( T_{BK} \). From lower to upper, the solid curves are results from the solution of the differential equations for \( A_{ds} = (1, 10, 100) \times A_3(T_c - T) \). The short-dashed and long-dashed curves are the bounds of Eqs. (17) and (18) respectively.

**FIG. 3.** Numerical and variational wall energies as functions of the dimensionless temperature \( \tau \). The vertical axis is scaled by the wall energy at \( T_{BK} \). From lower to upper, the solid curves are results from the solution of the differential equations for \( A_{ds} = (1, 10, 100) \times A_3(T_c - T) \). The short-dashed and long-dashed curves are the bounds of Eqs. (17) and (18) respectively.

Figure 3 shows the wall energy \( W \) as a function of temperature, as determined numerically for three different values of \( A_{ds} \); it shows also two variational approximations which we now obtain.

If we consider Eq.(14) as a trial function, with \( \kappa \) an adjustable parameter, we find

\[ W \leq e_{30}^3 \sqrt{3C_2 D_2/8} \]  

(17)

at the optimal \( \kappa \), namely \( \kappa = e_{30} \sqrt{3C_2/(8D_2)} \); the \( T \) dependence is in \( e_{30} \). From Figure 3, this does very well over the temperatures examined, not the least because it is an equality at \( T_{BK} \) for all \( A_{ds} \). The coefficients \( A_{ds} \) and \( D_3 \) do not appear because of the form of our trial function; explicitly, in obtaining Eq.(17), we did not drop the corresponding terms in the density, and so Eq.(17) is valid independent of the magnitude of the dilatational and shear energies and strains. Equation (17) seems to be an equality also in the limit \( A_{ds} \to \infty \) for all \( T \).

The wall energy was estimated previously, using the circular trajectory described above. On setting \( A_1 = A_6 = A_{ds} = 0 \), taking \( D_3 = D_2 \), and using \( e_3 = e_{30} \cos \phi \), \( e_2 = e_{30} \sin \phi \), with \( \frac{2\pi}{3} \leq \phi \leq \frac{4\pi}{3} \), we find

\[ W \leq \sqrt{64B_2 D_2 e_{30}^3/27} \]  

(18)

Unlike Eq.(17), this assumes that \( A_1 = A_6 = 0 \); including dilatation and shear only increases the value relative to Eq.(17). Figure 3 shows that Eq.(18) is considerably poorer than Eq.(17) for the temperatures examined; it is a factor of 3 larger at \( T_c \). But the trajectories bend toward the Hong-Olson arc at lower \( T \), and so Eq.(18) increases with decreasing \( T \) less strongly than Eq.(17) (as \( e_{30}^{5/2} \) rather than as \( e_{30}^3 \)). Indeed, for \( T < -151 \), Eq.(18) is actually better than Eq.(17); but this temperature may not be accessible since the strain there is \( \approx 10 \) times that at \( T_c \). For \( Fe_{70}Pd_{30} \), \( T = -151 \) is inaccessible (\( T < 0 \)).

In summary, we have found for the first time the solution for the C-T twin wall, at all \( T \), in the physical case with dilatational and shear energies and strains. The dilatation and shear strains, which are localized near the interface, change sign at \( T_{BK} \). The magnitudes (at most 1% in Fe-Pd alloys) may however be too small to detect.

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