Dynamics of Twin Boundaries in Martensites

G. R. Barsch,[(1)] B. Horovitz,[(1,2)(a)] and J. A. Krumhansl[(2)]
[(1)]*Materials Research Laboratory and Department of Physics, Pennsylvania State University, University Park, Pennsylvania 16802*
[(2)]*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853*
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The theory of forming a coherent twinning array in a parent phase is studied for a tetragonal-to-orthorhombic displacive transition. We find that this structure can be stabilized without the use of dislocations by a long-range interaction between the twin boundaries which is mediated via the parent phase. The dynamics of the twin boundary lattice consists of elementary excitations with surprisingly low frequency and a limiting dispersion of $\omega \sim k^{1/2}$.

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Formation of coherent alternating twins or domain structures is a common occurrence in structural and martensitic phase transitions.[1,2] The symmetry of the parent (untransformed) phase allows for formation of a few distinct variants or "twins" of the product (transformed) phase. The coexistence of two of these twins results in a localized twin boundary. The microscopic origin of the structural transition is of interest by itself and was recently summarized by one of us.[3]

It has been shown[4-7] that a static solution for a twin boundary or for a periodic array of twin boundaries can be produced entirely by displacive distortions of a high-symmetry phase without any need for dislocations. Explicit solutions were given in a continuum theory by allowing for both nonlinear elasticity and for nonlocal strains (i.e., strain gradients). The significance of this description, as will emerge below, is that large-scale motion at low frequency is allowed by the coherent twin boundary. This is very different from the dynamics of dislocations whose motion involves discontinuities in the strain field and hence drag and damping.

In the present work we study in particular a tetragonal to orthorhombic (T-O) transition. In addition to well-known examples such as In-Pb, Mn-Fe, and Mn-Ni[8] this transition and the related twin boundaries were recently observed in the copper-oxide high-T_c superconductors.[9-12] In a separate work[13] we show how the interactions between electrons and twin-boundary dynamics can be responsible for the observed enhancement of T_c; we also show there how other electronic properties and the heat capacity are affected. Besides relevance to high-T_c materials the anomalous high electronic specific heat of some heavy-fermion systems may be due to these interactions.

This T-O transition is essentially a two-dimensional square-to-rectangular transition. Since there are two ways to deform a square to a rectangle, the T-O transition has two twins related to each other by a reflection in the $\{110\}$ planes; the latter are also the allowed twin boundaries.[2] A detailed solution has been obtained from a Landau-Ginzburg free-energy expansion for the strain e_2,[5,7] keeping nonlinear terms and gradients of e_2. The extremum condition for the free energy yields a family of periodic solutions for a twin-boundary lattice (TBL) whose periodicity $2l$ varies in some finite range. Since the absolute ground state is a single variant, one needs an additional force in the system to stabilize the TBL and also to determine its periodicity.

The additional required force is provided by an interface between a parent phase and a twinned product phase, a configuration well known in martenistic transitions.[1,2,14] The geometry, as illustrated in Fig. 1, defines a habit-plane interface which intersects the twin boundaries. The intersection angle is determined such that the strain for parent-product matching (without dislocations) does not diverge. Twinning on the product side is then essential to allow for an equal *average* lattice constant on both sides of the habit plane, i.e., it is an invariant plane strain.[2,14] In this scenario the system is in a

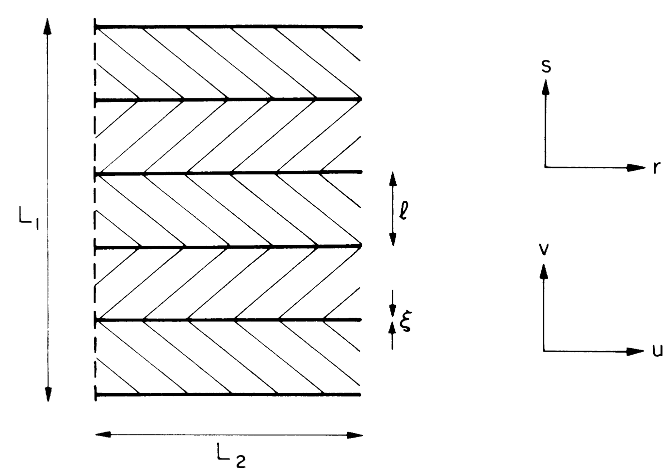

FIG. 1. Habit plane (dashed line) separates a twinned product phase (on right) from the parent phase (on left). L_1, L_2, and L_3 are dimensions of the product phase (L_3 is perpendicular to drawing). The separation between twin boundaries is l and their width is ξ. The [110] and [1$\bar{1}$0] directions are r and s, respectively, and the ion displacement fields are $u(r,s)$ and $v(r,s)$.

thermodynamically metastable state, the TBL being stabilized by a two-phase interface. Another type of interface is that between two perpendicular TBL's, as seen in some cases.[10-12] We expect the analysis below to be valid also for this case.

The evaluation of the strain energies proceeds in the following steps: First, the TBL is described by a one-dimensional modulation of a transverse displacement field $u(s)$.[5,7] We consider the case $l \gg \xi$ (see Fig. 1), and then a collective coordinate S_n for the position of the nth twin boundary can be defined. As usual in soliton theories,[15] we expect this "translation mode" coordinate to be well separated in frequency from the other degrees of freedom. As found below, this is indeed the case, at least for wave vectors $\gtrsim 1/L_2$. The displacement field is then

$$u(s) = -(-1)^n \epsilon(s-S_{n-1}) - \sum_{j=1}^{n-1} (-1)^j \epsilon(S_j - S_{j-1}) + \bar{u}, \quad S_{n-1} \le s \le S_n, \tag{1}$$

where $n=1,2,\ldots,M$, $\bar{u}=u(S_0)$, and the strain $e_2=[(\partial u/\partial s)+(\partial v/\partial r)]/\sqrt{2}$ relative to the tetragonal phase is $e_2=\pm\epsilon/\sqrt{2}$; the latter signs define the two possible twins. Define a small displacement coordinate δ_n from the expected ground-state position nl, i.e., $S_n = nl+\delta_n$. We assume an even number M of twin boundaries with boundary conditions $S_M=S_0+Ml$ and $u(S_M)=u(S_0)$, so that $\delta_0=\delta_M$ and $\sum_{n=1}^{M}(-1)^n\delta_n=0$. The values of l, $\bar{u}$, and δ_n are left as variational parameters. Thus, we focus on the essential "soft" coordinate part of the continuum solution without the need for its details or for the details of the free-energy functional.

The second step is to determine the habit plane by finding the invariant plane strain.[2,14] We find that the orientation of the habit plane is a sensitive function of ϵ and the volume ratio of the two twins. For simplicity we make one allowable choice that the habit plane is perpendicular to the twin boundaries; we have examined also other cases and the results below do not change qualitatively.

The third step is to determine the fringing elastic field for the displacements $u(r,s)$ and $v(r,s)$ in the parent phase. In the s direction we can assume periodic boundary conditions and define the Fourier components $u(r,k)$ and $v(r,k)$. For $r \to -\infty$, we can use linear elasticity theory, which yields

$$\begin{aligned} u(r,s) &= \textstyle\sum_k [u_1(k)e^{q_1 r} + u_2(k)e^{q_2 r}]e^{iks}, \\ v(r,s) &= \textstyle\sum_k [\beta_1 u_1(k)e^{q_1 r} + \beta_2 u_2(k)e^{q_2 r}]e^{iks}, \end{aligned} \tag{2}$$

with k real and $\mathrm{Re}\,q_i = \gamma_i |k| > 0$ $(i=1,2)$. The coefficients β_i, γ_i are $O(1)$ and determined by the elastic constants of the parent phase.

The final step is to match the solutions (2) and (1) across the habit plane. For simplicity we assume that ϵl is smaller than a lattice constant so that epitaxy-type discommensurations can be avoided. The parent-product matching is possible in principle, as guaranteed by the construction of the habit plane. We therefore extend (2) to $r=0$ and continuity with (1) yields $u_1(k), u_2(k) \sim u_0(k)$, where $u_0(k)$ is the Fourier transform of (1). While this is not an exact procedure for all k, we expect it to be accurate for the low-k components; the reason is that the resulting fringing field is of long range—expanding $u_0(k)$ with k and substituting in (2) yields $u(r,s), v(r,s) \sim 1/r$. This long-range field should not be sensitive to the details of the matching near the habit plane.

The interface elastic energy is now obtained by substituting (2) in the elastic energy and intergrating on $-\infty < r < 0$. The resulting integral on $\exp(\gamma_i |k| r)$ yields $\simeq |k|$ terms instead of the usual $\simeq k^2$ energies. The interface is then

$$E_{\mathrm{in}} = \alpha L_1 L_3 \textstyle\sum_k |k|\, |u_0(k)|^2, \tag{3}$$

where α is of the order of an elastic constant.

The elastic energy of the produce phase involves the creation energy E_0 of a twin boundary per unit area

$$E_{\mathrm{TB}} = E_0 L_2 L_3 L_1 / l\,[1+O(e^{-l/\xi})]. \tag{4}$$

Since the twin boundaries are exponentially localized in a width ξ[5,7] the interaction between them is $\simeq \exp(-l/\xi)$. This interaction can be neglected relative to (3) if $|k| L_2 \exp(-l/\xi) \ll 1$; for $l/\xi \simeq 20$–100[9-11] this is a safe assumption even for a macroscopic L_2. Substitution of (1) in (3) yields (for $\delta_n=0$ and $\bar{u}=-l\epsilon/2$) $E_{\mathrm{in}} = 0.27\alpha\epsilon^2 L_1 L_3 l$ which combined with (4) has a minimum at

$$l = [E_0 L_2/(0.27\alpha\epsilon^2)]^{1/2}. \tag{5}$$

The $\sqrt{L_2}$ dependence was derived previously,[16] although the method employed did not use the long-range effect in an obvious manner. Our analysis of twin bands resulting from the cubic-tetragonal transition in In-Tl[17] gives $l \simeq (L_2)^\sigma$ where $\sigma = 0.4$–0.5 consistent with Eq. (5); L_2 is in the range 2.7–10.5 μm.

We now address the fluctuations δ_n and their dynamics. Here we encounter the most important and surprising aspect of the twin structure. To grasp the basic idea, consider the motion of just one twin boundary, say $\delta_m \neq 0$ [Figs. 2(a) and 2(b)]. Since the strain e_2 in the twins is fixed at $\pm\epsilon$, the result is a displacement $u(s) \simeq \int_{S_m}^{s} ds' e_2(s')$ which affects the whole stack of twins with $s > S_m$. Thus, an apparently simple local motion of a boundary results in a coherent macroscopic motion [Fig. 2(a)].

To present this idea more precisely, consider the kinet-

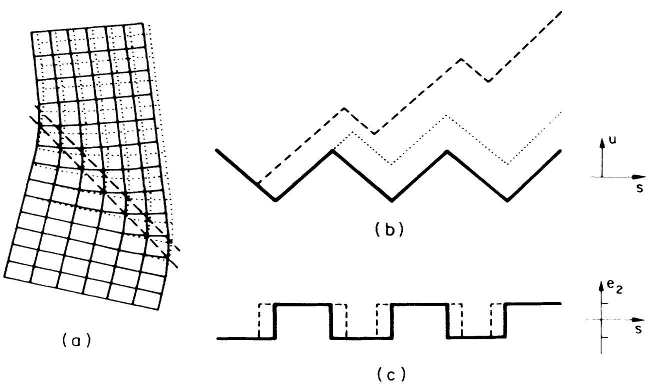

FIG. 2. Motion of twin boundaries. (a) Lower (upper) dashed line is a twin boundary separating the lattices with full (dotted) lines. Note that lattice sites shift perpendicular to the twin-boundary motion. (b) Displacement field $u(s)$ of a TBL (full line), the effect of the motion of a single boundary (dotted line), and the effect of a $q_1 \to 0$ oscillation (dashed line). (c) Strain e_2 of a TBL (full lines) and the effect of a $q_1 \to 0$ oscillation (dashed lines).

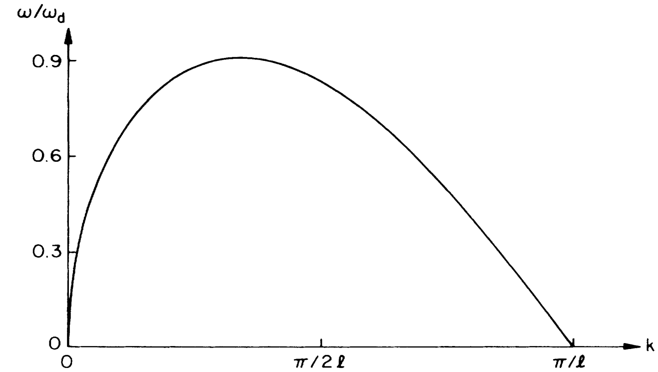

FIG. 3. Dispersion curve of twin-boundary oscillations —"dyadons" [Eq. (7)]. Note that in the reduced-zone scheme the Brillouin-zone boundary would be at $q = \pi/2l$.

ic energy of the product phase (the overhead dot is $\partial/\partial t$ and ρ is the mass density),

$$E_k = \tfrac{1}{2}\rho L_2 L_3 \int_{S_0}^{S_M} \dot{u}^2(s)\,ds = \tfrac{1}{2}\rho L_2 L_3 \epsilon^2 \sum_{n=1}^{M} \dot{\eta}_n^2, \qquad (6)$$

where the normal mode $\eta_n (n = 1, 2, \ldots, M)$ is $\eta_n = 2 \times \sum_{j=1}^{n-1} (-1)^j \delta_j + \delta_0 - \delta u$ and $\delta u = l/2 + \bar{u}/\epsilon$. The nonlocal transformation from δ_n to η_n implies that

$$E_k \sim \sum_k |\dot{\eta}(k)|^2 \sim \sum_k |\dot{\delta}(k)|^2 / \sin^2(\tfrac{1}{2}kl).$$

Thus the *effective kinetic mass* of the twin-boundary motion diverges as $k \to 0$, a most significant aspect of our results. It implies that possible damping due to coupling of localized lattice imperfections to δ_n vanishes as $k \to 0$.

The parent phase has a kinetic energy which by using (2) is smaller than (6) by a factor of $|k| L_2$. Thus, for $|k| \gg 1/L_2$ the elastic energy is dominated by the parent-product interface while the kinetic energy is dominated by the bulk product phase. This scenario has an analog in a linear elasticity problem; Love waves[18] describe localized waves in a layer of material A with thickness L_2 which is attached to a bulk material B. When the elastic constant of material A is vanishing, to mimic the above scenario, the dispersion of Love waves is[18] $\omega \simeq \sqrt{k}$ for $|k| \gtrsim 1/L_2$ [compare Eqs. (3) and (6)].

In our case Eq. (3) is valid only for describing the twin-boundary motion. In terms of $\eta(k)$, the Fourier transform of η_n, we find from Eqs. (3) and (6) the dispersion

$$\omega^2(k) = \omega_d^2 \sin^2(\tfrac{1}{2}kl) \sum_{p=-\infty}^{\infty} [\,|kl/2\pi - p|^{-1} - |\tfrac{1}{2} - p|^{-1}], \qquad (7)$$

where $\omega_d = (4\alpha/\pi\rho l L_2)^{1/2}$. This dispersion is shown in Fig. 3. For $k \to 0$, $\omega \simeq \sqrt{k}$, representing the long-range elastic force mediated through the parent phase. (Recall, however, that for $|k| L_2 \lesssim 1$, ω should become linear in $|k|$); the $k \to 0$ mode is shown in Figs. 2(b) and 2(c). Equation (7) has a zero mode also at $k = \pi/l$ which corresponds to a rigid translation of the whole twin-boundary lattice. The predicted frequencies are below $\omega_d \simeq \omega_{ac}(l/L_2)^{1/2}$, where ω_{ac} is an acoustic phonon with $q \simeq \pi/l$. For values of $l \simeq 100$–1000 Å and $L_2 \simeq 10^4$ Å [10-12] we estimate $\omega_d \simeq 10^{10}\ \mathrm{sec}^{-1}$.

To summarize, we have studied the statics and dynamics of coherent, reversible twin-boundary arrays. Since dislocations are avoided, the resulting dynamics corresponds to coherent low-frequency elementary excitations which involve a quasimacroscopic motion; we propose to call these excitations "dyadons." It is in fact known that by applying external stresses a large-scale reversible motion of habit planes and twin boundaries is possible.[19,20] The "shape memory effect"[21] which has been studied extensively is a manifestation of the motions discussed here; they are remarkable in that events on the atomic scale lead to a coherent, reversible, macroscopic effect.

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