AIP | Applied Physics Letters

# How to generate high twin densities in nano-ferroics: Thermal quench and low temperature shear

E. K. H. Salje, X. Ding, Z. Zhao, and T. Lookman

Citation: Appl. Phys. Lett. **100**, 222905 (2012); doi: 10.1063/1.4724192

View online: http://dx.doi.org/10.1063/1.4724192

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v100/i22

Published by the American Institute of Physics.

# How to generate high twin densities in nano-ferroics: Thermal quench and low temperature shear

E. K. H. Salje,[1,2] X. Ding,[1,3] Z. Zhao,[3] and T. Lookman[1]
[1]*Los Alamos National Laboratory, Theory Division and Centre for Nonlinear Studies, Los Alamos, New Mexico 87545, USA*
[2]*Department of Earth Sciences, University Cambridge, Cambridge CB2 3EQ, England*
[3]*State Key Laboratory Mechanical Behaviour of Materials, Xi An Jiao Tong University, Xian 710049, Peoples Republic of China*

(Received 2 May 2012; accepted 15 May 2012; published online 31 May 2012)

High domain boundary densities in ferroic nano materials are generated in computer simulation studies by (1) fast quench from a para-elastic into a ferroelastic phase and (2) by shear of small samples at low temperatures inside the stability field of the ferroelastic phase. Quenched samples evolve from tweed to junctions to stripe pattern. In driven systems, no tweed exists and the mesoscopic structure 'nucleates' rapidly when a yield stress is surpassed. The nucleated domain patterns are long-lived and change towards the single domain state only when the external strain is further increased. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4724192]

High twin boundary densities are required for applications where the functional elements of a device are the domain boundary and not the bulk. Interfaces and domain boundaries can contain structural elements, which are not a simple juxtaposition of adjacent bulk materials, which are the key for this functionality, including superconductivity, high ionic mobility, two-dimensional electron gas near compositional interfaces, usual vortices, and multiferroicity.[1–13] Such properties can be exclusively contained in the twin boundaries and do not exist in the bulk. In this situation, the twin walls qualify as objects in the emerging field of "domain boundary engineering"[14] where domain boundaries are optimized to specific functionalities, which remain localized in the domain boundaries. Typical nano materials with functional domain boundaries are perovskite structures ($WO_3$ and $CaTiO_3$)[1,15–17] and simple phase change materials (e.g., Cr:SnTe).[17] In magnetic devices, the analogous materials are nano wires in the IBM racetrack memory where moving magnetic domain walls act as active memory elements.[18] The wider industrial consequence of such local structures as memory devices, conductors, holographic templates, or as membranes for batteries has already motivated a large research effort over recent years. This paper aims to show how high twin densities can be achieved.

Two alternative routes are taken to produce high twin wall densities. First, domain structures nucleate in order-disorder systems when a sample is quenched rapidly from a high temperature, para-elastic phase into a ferroelastic phase. The reason for the formation of microstructures originates from the time evolution of the initial state, which contains thermal fluctuations of the local order parameter, and the subsequent nucleation of coarser microstructures. The second approach is to distort a single domain crystal by shear strain in the low temperature ferroelastic phase. In this way, a large number of long-lived metastable states are generated kinetically. This situation is encountered when thin films of one ferroelastic material are deposited onto another ferroelastic material at high temperatures. When the device is cooled to room temperature, the template will shear and impose this shear to the thin film. When this shear strain surpasses the yield strain, the thin film will spontaneously twin with a high twin boundary density. This pattern is then essentially stable under further shear. Driven systems[19] were used experimentally to generate high twin densities.[20,21]

When disorder is generated by structural rather than micro structural phenomena, one requires a source of disorder, which is commonly provided by local atomic disorder. In our case, we do not consider random fields, but start from uniform ground states. In this case, quench will freeze in some disorder in the para phase, which represents the initial state in the ferroelastic phase from where the microstructure evolves. Following Ref. 22, one can derive the structure factor of the displacement—displacement correlation in the simple case for $T > T_c$ and Ornstein-Zernike fluctuations

$$S_k \sim [1/r_c^2 + a^2\cos^2\Theta + b^2\sin^4\Theta\sin^2 2\varphi + gk^2]^{-1}$$

This function is a four-armed starfish in 3-dimension and represents the diffuse diffraction pattern in Fig. 1(a). The equivalent microstructure is tweed[22] that evolves into stripe patterns that have as structure factor dog's bones shown in Fig. 1(b).[23] The kinetic evolution is then for the quench experiment, the gradual change from the star to the dog's bone. Simple energy minimization of the relaxation in the stripe pattern for a finite sample and the interfacial energy of the twin walls (~g) lead to the Kittel law[24]

$$w \sim L^{1/2}$$

where w is the distance between the twin walls and L is the sample size. Typical examples are elastically soft $Pb_3(PO_4)_2$, which forms stripes under quench while the harder $Pb_3(AsO_4)_2$ forms a denser microstructure with intersection domain boundaries.[29]

The alternative route to highly twinned materials is by hard driving (where the strain is prescribed) of a sample in the ferroelastic state. Increasing strain leads to a collapse of the mono domain state above the yield stress into a highly

 

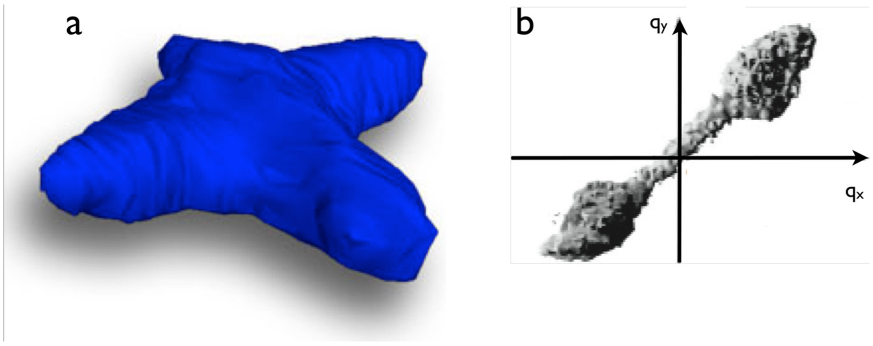


FIG. 1. The kinetic effect of annealing tweed pattern with a four-armed starfish-type structure factor $T > Tc$ (a) to a stripe pattern with a dog's bone structure (b). These experimental examples were taken from cuprate superconductors[25] and highly twinned $LaAlO_3$.[26]

structured, mesoscopic twin pattern without the previous nucleation of a tweed structure. The model to describe this displacive collapse of the shear structure was proposed by Salje *et al*.[27] We use their model to simulate the shear instability in a 2-dimensional monoatomic lattice. The second nearest neighbor interaction were adjusted to yield as ground state a sheared lattice with shear angles $\pm 4°$. The external driver is a shear strain at the upper and lower edge of the sample, which stabilizes one domain orientation ($+4°$) and destabilizes the other ($-4°$). Increasing strain is initially compensated by an elastic deformation until a threshold is reached where the unstable domain decomposes into a multitude of twinned micro domains (Fig. 2). The stress-strain curves and the domain patterns depend sensitively on the size of the system and on the elastic moduli of the sample. We tested a hard material (nearest neighbor spring constant $k_1 = 20$) and a soft material ($k_2 = 10$). The hard material displays a small number of vertical domains and few horizontal domain walls (Fig. 2 right panel). The soft material has a much more complex domain pattern with a large number of vertical walls and some horizontal walls (Fig. 2 left panel).

The mechanical response of the thin layer shows the typical criticality for shear strains of ca. $3.3 \times 10^{-4}$ and a collapse of the stress from the upper yield stress to the lower yield stress by some 75% for large systems. The geometrical analysis of this decay contains a network of intersecting twin boundaries, which are destroyed when the stable domain invades the unstable region that is not tweed-like, but contains locally well-defined twin boundaries and their intersections. These form complex pattern, their structure factor is shown in Fig. 3. The noise pattern during shear in the hard material follows a power law statistics with the probability of a noise jerk of energy E to be $P(E) \sim E^{-\varepsilon}$ with energy exponents $\varepsilon \approx 2$, the waiting time statistics follows a power law correlated for hard material, which indicates correlations between the jerks.[28]

The strain-induced twinning leads to very stable configurations where the domain boundaries inside the unstable region get hardly changed under further strain, all dynamics is dominated by the progressing front of the large stable domains on the top and the bottom of the sample. A convenient parameter to characterize "complexity" is the number density of intersections between different twin walls. We call these intersections, in accordance with previous experimental observations, "junctions," so that the junction density becomes the key parameter to describe the complexity of our

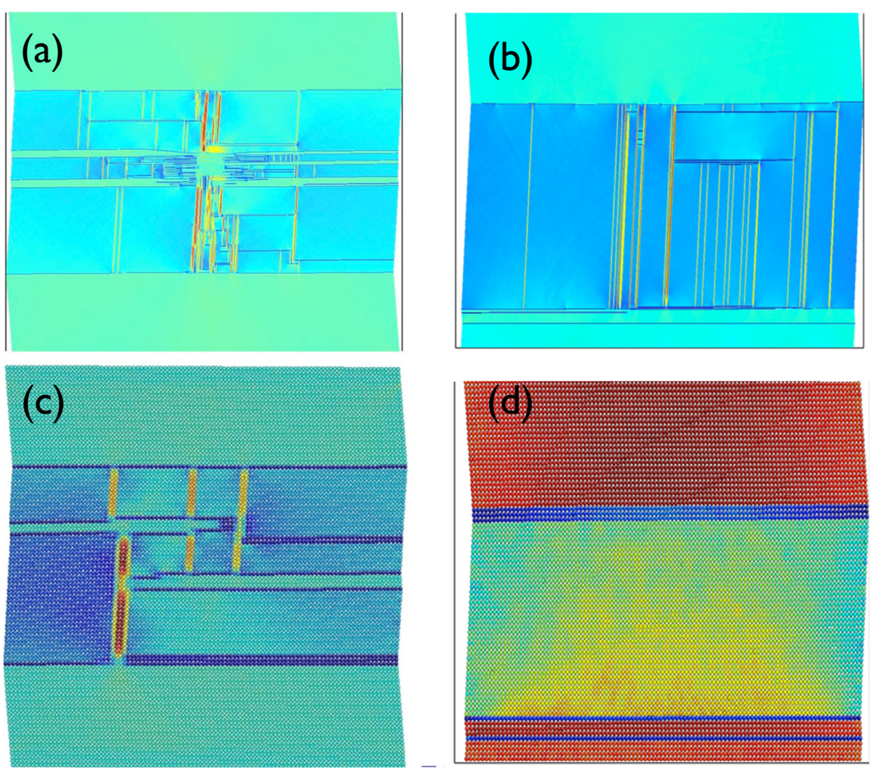


FIG. 2. Domain pattern formed after the collapse at the yield stress for a large system with $10^6$ atoms (a) and (b) and small system (10 200 atoms) (c) and (d). The images (a) and (c) represent soft systems while (b) and (d) show hard systems (the colors refer to the local shear angles $|\Theta_{vertical} - 4°| + \Theta_{horizontal}$, see Ref. 27).

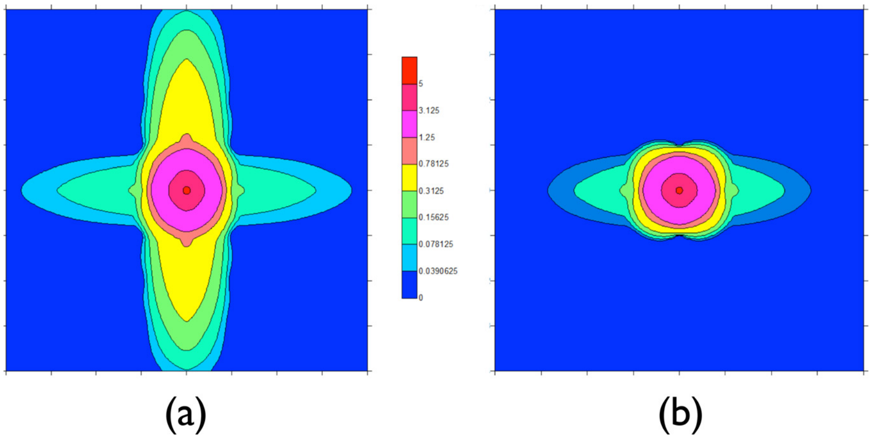


FIG. 3. (a) and (b) Diffuse scattering of strain induced microstructures for a sample with $10^6$ atoms and soft nearest neighbor interactions. The range is from $-0.04$ to 0.04 reciprocal units. The soft system is shown in (a) and the hard system in (b). Note the slimmer arms of the starfish, as compared with the quenched sample in Fig. 1(a). The stronger concentration of the diffuse scattering originates from the stricter confinement of the twin domains along the elastically soft directions and the smaller number of junctions compared with tweed pattern. The same conditions for a sample with "hard" elastic interactions (b) shows the predominance of one domain orientation and fewer twin walls.

twin patterns. Different tendencies were found for hard and soft materials. The hard materials have fewer junctions and the junction density ($10^{-4}$ for $10^6$ atoms) disappears for small systems when the sample cannot support complex patterns. In contrast to hard materials, we find that soft materials contain generally more complex twin pattern with higher junction densities ($5 \times 10^{-3}$ for $10^6$ atoms). The junction density increases with smaller system sizes where the strong relaxation of the systems allows the formation of junctions even for very small samples before they collapse for systems with fewer than 100 atoms. This shows that the desired materials properties for domain boundary engineering with high boundary and junction densities are best achieved for soft materials. Furthermore, small system sizes do not impede the formation of twin walls but, on the contrary, enable them. Small particles will show twinning in soft materials, but not in hard ferroelastics. In conclusion, we find that high wall and junction densities can be achieved when the thin film samples are driven by rapid quench or by shear deformation. The internal structures are different, however, quenched samples are less complex and show tweed or stripe patterns while sheared samples show complex twinning with high junction densities.

[1]A. Aird and E. K. H. Salje, J. Phys.: Condens. Matter **10**, L377 (1998).
[2]Y. Kim, M. Alexe, E. K. H. Salje, Appl. Phys. Lett. **96**, 032904 (2010).
[3]J. Seidel, P. Maksymovych, Y. Batra, A. Katan, S.-Y. Yang, Q. He, A. P. Baddorf, S. V. Kalinin, C.-H. Yang, J.-C. Yang, Y.-H. Chu, E. K. H. Salje, H. Wormeester, M. Salmeron, and R. Ramesh, Phys. Rev. Lett. **105**, 197603 (2010).
[4]M. Calleja, M. T. Dove, and E. K. H. Salje, J. Phys.: Condens. Matter **15**, 2301 (2003).
[5]A. Ohtomo and H. Y. Hwang, Nature (London) **427**, 423 (2004).
[6]S. A. Pauli, S. J. Leake, B. Delley, M. Bjorck, C. W. Schneider, C. M. Schlepütz, D. Martoccia, S. Paetel, J. Mannhart, and P. R. Willmott, Phys. Rev. Lett. **106**, 036101 (2011).
[7]M. Huijben, G. Rijnders, D. H. A. Blank, S. Bals, S. Van Aert, J. Verbeeck, G. Van Tendeloo, A. Brinkman, and H. Hilgenkamp, Nature Mater.**5**, 556 (2006).
[8]B. Kalisky, J. R. Kirtley, J. G. Analytis, J.-H. Chu, I. R. Fisher, and K. A. Moler, Phys. Rev. B **83**, 064511 (2011).
[9]Y. Ivry, D. Chu, J. F. Scott, E. K. H. Salje, and C. Durkan, Nano Lett. **11**, 4619 (2011).
[10]T. Birol, N. A. Benedek, and C. J. Fennie, Phys. Rev. Lett. **107**, 257602 (2012).
[11]A. Lubk, S. Gemming, and N. A. Spaldin, Phys. Rev. B **80**, 104110 (2009).
[12]T. Lottermoser and M. Fiebig, Phys. Rev. B **70**, 220407 (2004).
[13]S. Conti, S. Muller, A. Poliakovsky, and E. K. H. Salje, J. Phys.: Condens. Matter **23**, 142203 (2011).
[14]E. K. H. Salje, ChemPhysChem **11**, 940 (2010).
[15]S. Van Aert, S. Turner, R. Delville, D. Schrvyers, G. Van Tendeloo, and E. K. H. Salje, Adv. Mater. **24**, 523 (2012).
[16]X. F. Wu, K. M. Rabe, and D. Vanderbilt, Phys. Rev. B **83**, 020104 (2011).
[17]E. K. H. Salje, D. J. Safarik, K. A. Modic, J. E. Gubernatis, J. C. Cooley, R. D. Taylor, B. Mihaila, A. Saxena, T. Lookman, J. L. Smith *et al.*, Phys. Rev. B **82**, 184112 (2010).
[18]S. P. Parkin, M. Hayashi, and L. Thomas, Science **320**, 190 (2008).
[19]F. J. Perez-Reche, L. Truskinovsky, and G. Zanzotto, Phys. Rev. Lett. **101**, 230601 (2008).
[20]R. J. Harrison and E. K. H. Salje, Appl. Phys. Lett. **97**, 021907 (2010).
[21]C. M. Gallardo, J. Manchado, F. J. Romero, J. del Cerro, E. K. H. Salje, A. Planes, E. Vives, R. Romero, and M. Stipcich, Phys. Rev. B **81**, 174102 (2010).
[22]A. M. Bratkovsky, S. C. Marais, V. Heine, and E. K. H. Salje, J. Phys.: Condens. Matter **6**, 3679 (1994).
[23]E. Salje and K. Parlinski, Supercond. Sci. Technol. **4**, 93 (1991); K. Parlinski, V. Heine, and E. K. H. Salje, J. Phys.: Condens. Matter **5**, 497 (1993).
[24]A. Schilling, T. B. Adams, R. M. Bowman, J. M. Gregg, G. Catalan, J. F. Scott, Phys. Rev. B **74**, 024115 (2006); G. Catalan, H. Bea, S. Fusil, M. Bibes, P. Baruch, A. Barthelemy, and J. F. Scott, Phys. Rev. Lett. **100**, 027602 (2008).
[25]K. R. Locherer, S. A. Hayward, P. J. Hirst. J. Chrosch, M. Yeadon, J. S. Abel, and E. K. H. Salje, Philos. Trans. R. Soc. London, Ser A **354**, 2815 (1996).
[26]J. Chrosch and E. K. H. Salje, J. Appl. Phys. **85**, 722 (1999).
[27]E. K. H. Salje, X. Ding, Z. Zhao, A. Saxana, and T. Lookman, Phys. Rev. B **83**, 104109 (2011).
[28]K. A. Dahmen, Y. Ben-Zion, and J. T. Uhl, Nat. Phys. **7**, 554 (2011).
[29]U. Bismayer and E. Salje, Acta Cryst. A **37**, 145 (1981); E. K. H. Salje, A. Graemebarber, M. A. Carpenter, and U. Bismayer, Acta Cryst. **49**, 387 (1993).