

Accurate determination of orientation relationships between ferroelastic domains: the tetragonal to monoclinic transition in LaNbO₄ as an example.

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ABSTRACT

LaNbO₄ crystallizes in a tetragonal high-temperature phase with space group I4₁/a, which transforms to a monoclinic phase upon cooling below 500 °C. The low-temperature phase has space group I2/a (C2/c) with a monoclinic angle $\beta=94.1^\circ$. This system serves as a useful model of a ferroelastic transition of the 4/mF2/m type using the notation of Aizu [1]. This transition produces ferroelastic domains, the boundaries between which are parallel to the monoclinic b-axis. The orientation of these boundaries relative to the monoclinic a- and c-axes has been predicted by Sapriel [2] for all 94 ferroelastic species, and calculations specifically for the LaNbO₄ system have been presented by Jian and Wayman [3].

We present an accurate determination of the boundary orientation in LaNbO₄ using selected area electron diffraction. The boundary planes are parallel to the (2 0 -5.10)/(5.10 0 2) planes of the two domains, as opposed to the predictions of Jian and Wayman which indicate that the domain boundaries should be oriented parallel to the (2 0 -4.04)/(4.04 0 2) planes. Our experimental results are in good agreement with the results of a previous study [4].

Furthermore, we present a simple geometric model for calculating the boundary orientation based only on the unit cell parameters of the monoclinic phase. This model gives a boundary orientation in excellent agreement with our experimental determination.

INTRODUCTION AND THEORY

Ferroelastic theory

Ferroelectric or ferromagnetic materials display an electric or magnetic polarization even in the absence of external electric or magnetic fields, and are generally referred to as *ferroic* crystals. By applying an external field, this spontaneous polarization can be switched between different allowed orientation states. A third group of crystals is also part of this general class, they are referred to as the *ferroelastic* crystals. In complete analogy to the ferroelectric and ferromagnetic systems, these are crystals which, in the absence of external mechanical stress, possess a spontaneous strain tensor. By applying a mechanical stress, the crystal can change from one orientation state to another, thereby changing the spontaneous strain tensor.

Aizu has described the 773 different species of ferroic crystal [1], and determined the orientation states and spontaneous strain tensors for the 94 species of ferroelastic crystals [5].

The origin of the ferroelastic orientation states is a structural phase transition from one crystal structure to another. Due to the symmetry of the structure before transformation, there may be several equivalent ways for such a transition to occur. As an example, we may consider the transformation from a cubic to a tetragonal system: here, any one of the three unit cell axes may elongate or contract to produce the tetragonal structure, see Figure 1.

These three ways of transforming produce the same result: the orientation states are crystallographically and energetically equivalent. This makes it impossible to distinguish one from the other if they appear separately. In most cases, however, a crystal is likely to exhibit more than one orientation state, and it will then be possible to distinguish them. This applies to all ferroic systems.

A region of a sample consisting of a specific orientation state is called a domain, and the boundary between two domains is called the domain wall or domain boundary. Not all domain wall orientations are favourable, the walls will, whenever possible, be oriented so as to maintain strain compatibility between the two neighbouring domains. Sapriel [2] has formulated the domain-wall equations for the ferroelastic species.

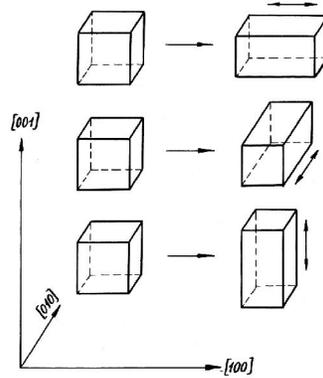


Figure 1: Three equivalent ways of transforming from a cubic to a tetragonal unit cell. These three orientation states have identical crystal structure, but are not related through an operation of symmetry of the tetragonal phase.

We give a short summary of some important properties of the ferroelastic crystals, see Aizu [1], [5] and Sapriel [2]. One may note that many of these properties apply also for other ferroic systems.

1. The ferroelastic crystals are a result of a transition from a high-symmetry *prototypic* phase to a low(er)-symmetry *ferroic* phase. This transition induces the formation of at least two *orientation states*.
2. The orientation states are identical or enantiomorphic in structure, and therefore energetically equivalent. They are, however, different in spontaneous strain tensor.
3. We denote the strain tensor of an orientation state S_i as $e(S_i)$. Schlenker et al. [6] have shown how the components of this strain tensor can be calculated from the lattice parameters of the crystal before and after the transition from the prototypic to the ferroelastic phase.
4. A ferroelastic crystal can change from one orientation state to another by the application of external mechanical stress.
5. If S_1, S_2, \dots, S_q are the q orientation states of a crystal, the *spontaneous* strain tensor of an orientation state S_i is defined by Aizu [5] as:

$$e_s(s_i) = e(s_i) - \frac{1}{q} \sum_{k=1}^q e(S_k) \quad (1)$$

6. The prototypic phase is said to belong to the point group L_p , while the ferroelastic phase belongs to the point group L_f with lower symmetry. L_f is a subgroup of L_p , i.e. L_p contains all the symmetry elements of L_f . We denote the elements of L_p which are not contained in L_f as F . That is:

$$L_f \subset L_p$$

$$F = (L_f \cap L_p)^c \quad (2)$$

7. All operations of L_f keep the strain tensors, e and e_s , unchanged, and therefore the orientation state is unchanged under these operations. The operations contained in F , however, cause a change from one orientation state to another. The orientation states are therefore related through the operations of symmetry lost in the transition from the prototypic to the ferroelastic phase.

8. The boundary between two domains - the domain wall - is oriented so as to maintain strain compatibility between the two domains. More precisely speaking, we assume that the boundaries are planes containing vectors which during the transformation from the prototypic to the ferroelastic phase change an equal amount in both orientation states. Sapriel [2] has expressed this mathematically as:

$$(S_{ij} - S'_{ij})x_i x_j = 0 \quad (3)$$

Here S_{ij} and S'_{ij} are the components of the spontaneous strain tensor of the orientation states labeled S and S' . Similarly, x_i and x_j are the components of a vector \mathbf{x} . Working from these conditions, Sapriel has determined the equations of all possible domain walls for the 94 species of ferroelastic crystals.

The case of ferroelastic LaNbO₄

LaNbO₄ is known to have two polymorphs. At high temperatures it has a tetragonal structure with space group I4₁/a [7] (no. 88), while the low temperature phase is monoclinic with space group I2/a (C2/c, no. 15) [8], see table 1. The phase transition is of the second order and occurs at approximately 500 °C.

During the transition, one unit-cell edge contracts, while another elongates. At the same time the angle between them increases from 90° to 94.1°. The change in the third (monoclinic) axis is rather insignificant. Due to the fourfold rotation symmetry of the tetragonal phase, there are four possible choices of how the changes in cell parameters can occur. After the transition, the fourfold symmetry is replaced by a twofold symmetry, and the four choices are then pairwise related through the rotation symmetry of the monoclinic cell. This leaves two *orientation states*, the lattices of which are *not* related through this symmetry, even though they are crystallographically equivalent, see Figure 2. They are instead related through an arbitrary rotation about the [010] axis. This transition is called a 4/mF2/m ferroelastic transition using the notation of Aizu.

Table 1: The cell parameters of the tetragonal and monoclinic phases of LaNbO₄ [9].

	a/Å	b/Å	c/Å	α	β	γ	Space group	Point group
Tetragonal	5.4 0	5.40	11.6 7	90.0 °	90.0 °	90.0°	I4 ₁ /a	4/m
Monoclinic	5.5 7	11.5 3	5.20	90.0 °	94.1 °	90.0°	I2/a	2/m

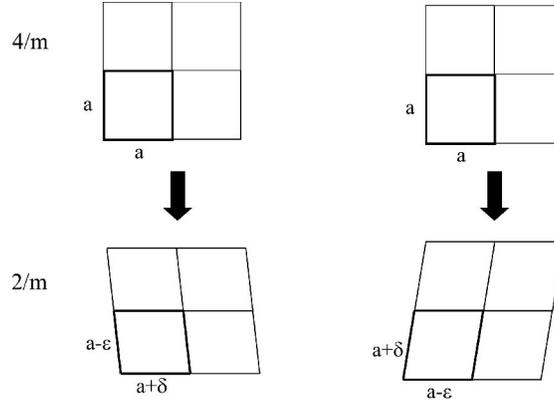


Figure 2: The two orientation states for the $4/mF2/m$ ferroelastic transition. Note that the two orientation states are crystallographically equivalent. They are related through a fourfold rotation in the tetragonal phase, but neither a fourfold nor a twofold rotation in the monoclinic phase.

Using the formalism of Sapriel as sketched above, the orientation of the boundaries between the ferroelastic domains in LaNbO_4 may now be determined. This calculation is rather involved, and requires knowledge of the cell parameters of both the tetragonal and monoclinic phases. Jian and Wayman [3] performed these calculations, and arrived at a boundary running parallel to the monoclinic b axis with a predicted orientation of $(2\ 0\ -4.04)/(4.04\ 0\ 2)$.

EXPERIMENTAL RESULTS

Performing high resolution electron microscopy in the $[010]$ projection, we observe the domain boundary edge on, see Figure 3a. The boundary region appears highly ordered, and we create a model of the atomic arrangement near the boundary, Figure 3b and c. This model indicates that the domain boundary is the $(2\ 0\ -6)/(6\ 0\ 2)$ plane.

We obtain a more accurate determination of the domain boundary orientation, from a selected area electron diffraction pattern in the $[010]$ projection, see figure 4. We note a characteristic splitting of virtually all the diffraction spots, indication that the lattices of the two domains are related through a simple rotation about the $[010]$ axis of about 95° , consistent with what we would expect for ferroelastic domains of this type.

The domain boundary is plane with the same orientation in both domains, and can be identified by a lack of splitting of the corresponding reflections. In Figure 4, there are two sets of spots that apparently satisfy this requirement, those corresponding to the $(2\ 0\ -4)/(4\ 0\ 2)$ and $(2\ 0\ -6)/(6\ 0\ 2)$ planes. This would be in good agreement with our HREM observations. However, careful examination of the diffraction pattern reveals that these reflections are split as well.

Tilting the sample somewhat out of the $[010]$ projection, we are able to observe higher index reflections, providing us with more accurate information, Figure 4c. Careful examination of the geometry of the diffraction pattern in the vicinity of the $(4\ 0\ -10)/(10\ 0\ 4)$ reflections reveal a slight, but significant, splitting of this reflection, see Figures 4d and e. The exact intersect of the reciprocal lattices of the two domains can be calculated using a simple geometric relation and measuring the splitting of the adjacent reflections, d_1 and d_2 :

$$l = 2c^* + \frac{4c^*}{\kappa d_1 + \kappa d_2} \kappa d_1 \quad (4)$$

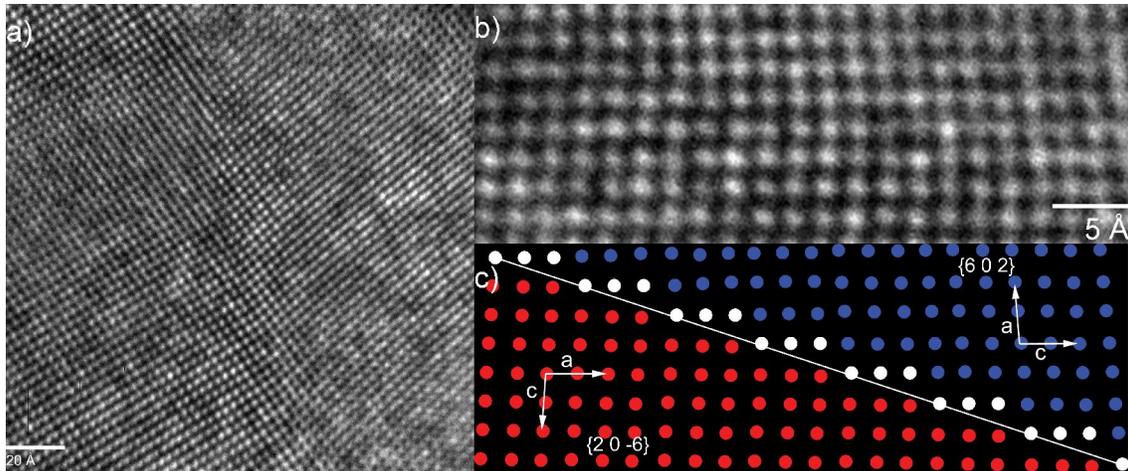


Figure 3: a) HREM micrograph of a domain boundary obtained in the [010] projection. b) Close up of a part of the domain boundary. c) Model of the atomic arrangement in the vicinity of the boundary.

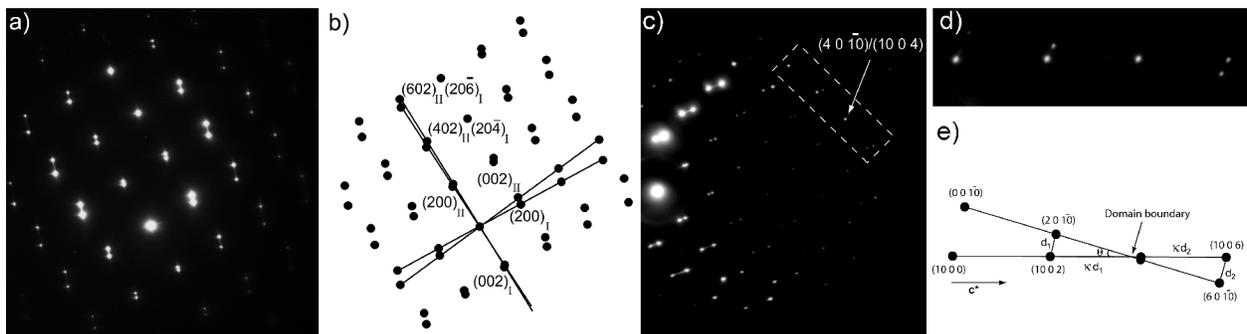


Figure 4: a) SAED pattern from a boundary region obtained in the [010] projection. b) Indexing of the diffraction pattern in a. c) Diffraction pattern obtained with the sample tilted somewhat out of the [010] projection. d) Close up of the region indicated in c. e) Sketch of the arrangement of reflections in the diffraction pattern in d.

This gives an observed orientation of the domain boundary parallel to $(2\ 0\ -5.10)/(5.10\ 0\ 2)$, which differs considerably from the orientation predicted by Jian and Wayman.

DISCUSSION AND CONCLUSION

We have seen that the domain boundary orientation predicted by Jian and Wayman using the formalism of Aizu and Sapriel differs considerably from the experimentally determined orientation. We therefore consider a simple model of the lattice geometry at the domain boundary in order to predict the orientation, see Figure 5. We realize that the domain boundary is the diagonal of Figure 5, and must be equal in length when viewed from either domain. This gives us a simple geometric relation for determining the orientation of the boundary in terms of the parameter k as indicated in Figure 5:

$$k = \frac{-4ac \cos \beta \pm \sqrt{4a^2c^2 \cos^2 \beta - 2a^2c^2 + a^4 + c^4}}{a^2 - c^2} \quad (5)$$

In this model, the orientation of the domain boundary depends only on the cell parameters of the monoclinic phase. Using the cell parameters tabulated in table 1, we calculate a domain boundary orientation of $(2\ 0\ -5.01)/(5.01\ 0\ 2)$, which is very close to the experimentally determined orientation $(2\ 0\ -5.10)/(5.10\ 0\ 2)$.

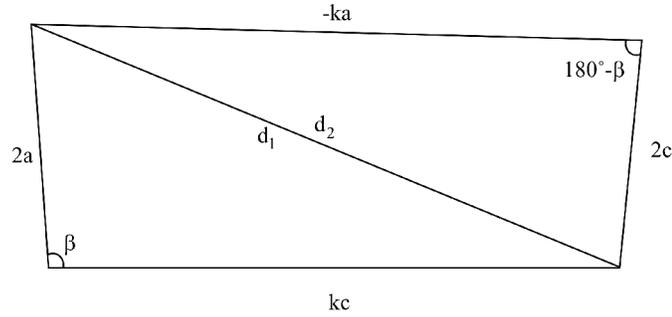


Figure 5: The orientation of the domain boundary with respect to the crystal on either side of the boundary. Based on this sketch, the orientation of the boundary can be elucidated based on the monoclinic cell parameters.

To conclude, we have studied the orientation of ferroelastic domain boundaries in LaNbO_4 using high resolution electron microscopy and selected area electron diffraction at room temperature. The observed orientation is parallel to the $(2\ 0\ -5.10)/(5.10\ 0\ 2)$ planes of the two domains. The orientation predicted by ferroelastic theory differs considerably from this, while predictions made using a simple geometric model are in excellent agreement with the observed orientation.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Drs. Y. M. Baikov and B. T. Melekh of the Ioffe Physico-Technical Institute, St. Petersburg, Russia, and Professor Truls Norby of the Department of Chemistry, the University of Oslo for providing the materials used in this study.

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