Mechanisms for the reconstructive phase transition between the $B1$ and $B2$ structure types in NaCl and PbS

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Three possible mechanisms for the reconstructive phase transition from the $B1$ to the $B2$ structure types are examined: (1) a modified Buerger (MB) pathway, (2) the Watanabe (W) pathway, and (3) a new pathway (T) proposed by Tolédano *et al.* [Phys. Rev. B **67**, 144106 (2003)]. We use first-principles energy calculations to obtain barrier heights for these pathways in NaCl and in PbS. In both NaCl and PbS, the barriers for the MB and T pathways are approximately equal. In NaCl, the barrier for the W pathway is somewhat higher. Both the MB pathway and the T pathway pass through an intermediate $B33$ structure type. As a result, the fact that a stable B33 intermediate structure is actually observed in PbS does not favor the T pathway over the MB pathway. We also examine experimentally obtained relations between the orientations of the $B1$ and $B2$ structures and conclude that they do not definitively favor any pathway over the others.

I. INTRODUCTION

A large class of structural phase transformations in solids is reconstructive, i.e., no group-subgroup relation between the symmetries for the initial and final structures and a change in the nearest-neighbor coordination number. However, our understanding of reconstructive transformation pathways and their energy barriers is very limited, even in the relatively simple case of $B1$ (NaCl-type), space group 225 $Fm\bar{3}m$, to $B2$ (CsCl-type), space group 221 $Pm\bar{3}m$, transition. It is not obvious which path each atom takes from its position in $B1$ (coordination number 6) to its position in $B2$ (coordination number 8). One usually assumes that the atoms throughout the crystal are displaced simultaneously and coherently so that, at least locally, the structure of the crystal as it moves from $B1$ to $B2$ is well defined and characterized by a space-group symmetry. For many years, the two major proposed pathways for the $B1$-$B2$ transition has been the Buerger (B) pathway[1,2] and the Watanabe (W) pathway.[3,4] Recently, two additional pathways have been proposed.

(1) Stokes and Hatch[5] showed with first-principles energy calculations that the energy barrier for the Buerger pathway could be lowered in NaCl by introducing a monoclinic distortion along the path. We call this the modified Buerger (MB) pathway. Recently, Catti[6] showed (also with first-principles energy calculations) that as CaO moves along this MB pathway from $B1$ to $B2$, the crystal passes through an intermediate metastable TlI-like orthorhombic structure ($B33$ structure type).

(2) Tolédano *et al.*[7] proposed a new pathway. They were motivated by an experimentally observed intermediate $B33$ structure in the $B1$-$B2$ phase transition in PbS. We call this the Tolédano (T) pathway.

We will show that the T pathway is simply a variation of the W pathway and that the intermediate $B33$ structures in the MB pathway and in the T pathway are identical. We will also show from first-principles energy calculations that the

MB and the T pathways are approximately equally energetically favorable, both in NaCl and in PbS. Finally, we will examine experimentally obtained relations between the orientations of the $B1$ and $B2$ structures and find that they do not definitively favor any pathway over the others.

II. PATHWAY DISCUSSION

In the W pathway (Fig. 1), alternating (001) planes of atoms in $B1$ are displaced in the [110] direction. In returning to the $B1$ structure, alternating (110) planes of atoms in the $B2$ structure are displaced in the [001] direction. The symmetry of the structure as it evolves from $B1$ to $B2$ is orthorhombic with space group 59 $Pmmn$.

The T pathway is shown in Fig. 2 and involves the same planes of atoms being displaced in the same directions as in the W pathway. (For this reason, the W and T pathways cannot be distinguished using experimentally obtained orientation relations between the $B1$ and $B2$ structures.) In the T pathway, however, alternating *pairs* of (001) planes of atoms
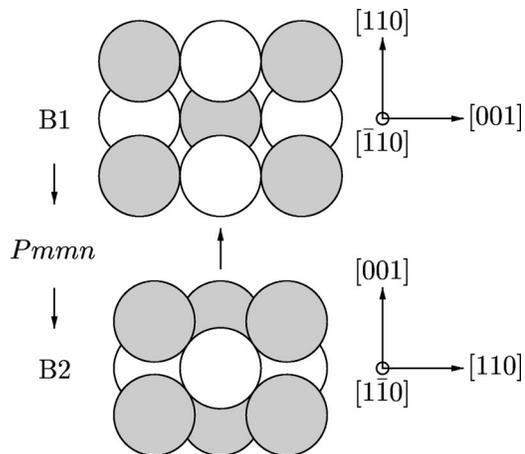

FIG. 1. Watanabe pathway from $B1$ to $B2$. The center plane of atoms moves upward.
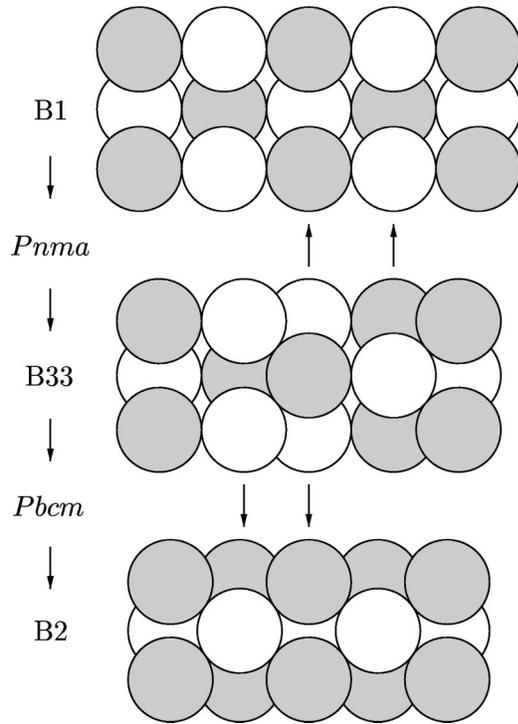
FIG. 2. Tolédano pathway from $B1$ to $B2$. First, two planes of atoms move upward, and then a different two planes of atoms move downward.

in $B1$ are displaced in the [110] direction. This results in an intermediate $B33$ structure with space group 63 $Cmcm$. Then, a different set of alternating pairs of planes of atoms are displaced, finally bringing the structure to $B2$. If we number adjacent planes of atoms 123412341234 . . . , then in step 1, planes 3 and 4 move together, and in step 2, planes 2 and 3 move together. The symmetry of the structure between $B1$ and $B33$ is space group 62 $Pnma$, and between $B33$ and $B2$ is space group 57 $Pbcm$, as indicated in the figure.

The MB pathway is shown in Fig. 3. The structures are displayed with the same crystalline orientation as in Figs. 1 and 2. The phase transition along this pathway is driven by strain. The figure shows how the unit cell defined by the intermediate $B33$ structure evolves from $B1$ to $B2$. The $B33$ structure appears as the unit cell in the figure passes through a rectangular shape. We also see that as the structure evolves from $B1$ to $B33$, the atoms in planes 2 and 4 (using the above notation) must move slightly upward relative to the unit cell shown. As the structure evolves further to $B2$, those planes of atoms move back to their original positions, again relative to the unit cell shown.

In comparing Fig. 3 with Fig. 2, we see common features which were unexpected. The MB pathway is mainly driven by strain. The T pathway is mainly driven by atomic shuffles. And yet these two pathways are very similar, sharing even the same intermediate structure $B33$. The $B33$ structure is stable in PbS and has been experimentally observed:[8] the two pressure-driven transitions $B1$ to $B33$ and $B33$ to $B2$ occur at about 2.3 and 22.5 GPa, respectively. Tolédano *et al.*[7] used the appearance of $B33$ in PbS (and in a few other related compounds) as evidence for their proposed pathway. How-
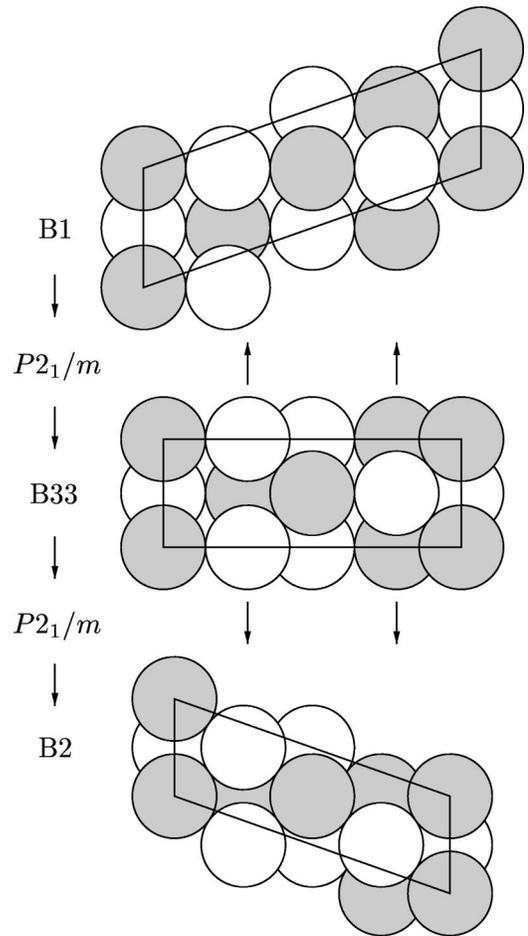

FIG. 3. Modified Buerger pathway from $B1$ to $B2$. Strain changes the shape of the unit cell shown. Also two planes first move upward with respect to the unit cell and then downward again.

ever, we see that the mere appearance of $B33$ does not distinguish between the T and MB pathways.

In Table I, we give details about the structures in the three pathways.

III. ENERGY BARRIERS

We calculated the energy barrier for each pathway in NaCl and in PbS using VASP, a first-principles density-functional theory (DFT) method, which is implemented with plane-wave basis sets,[9] ultra-soft pseudopotentials,[10] and the local-density approximation (LDA) to the exchange-correlation interaction. The cutoff energies of the plane-wave bases are 220 eV and 198 eV for NaCl and PbS respectively. The integration over the Brillouin zones were carried out by summing k points over Monkhorst-Pack grids. Careful tests have been done to ensure the numerical convergences for the k-point samplings and plane-wave cutoffs.

Ab initio LDA calculations are known to provide excellent predictions of structural properties of solids. For example, our calculated lattice constants of the $B1$ structures of NaCl and PbS are 5.462 Å and 5.855 Å, respectively, which are in close agreement with the previous calculations of Chall *et al.*[11] and Lach-hab *et al.*[12] Our, and previous, LDA lattice

TABLE I. Common subgroups for structures along the Watanabe (W), Tolédano (T), and modified Buerger (MB) pathways. We list (1) the space-group symmetry of the common subgroups G' of the structures G, (2) the lattice vectors of G' in terms of the lattice vectors of G, and (3) the Wyckoff positions of the atoms in G'. The parameters δ_1, δ_2 account for the small atomic displacements along the b axis in $B33$.

Path	G'	G	Lattice	Na (Pb)	Cl (S)
W	59 $Pmmn$	B1	$(0,0,1),(-\frac{1}{2},\frac{1}{2},0),(-\frac{1}{2},-\frac{1}{2},0)$	$(a)\ \frac{1}{4},\frac{1}{4},\frac{3}{4}$	$(b)\ \frac{1}{4},\frac{3}{4},\frac{1}{4}$
		B2	$(1,1,0),(1,-1,0),(0,0,-1)$	$(a)\ \frac{1}{4},\frac{1}{4},1$	$(b)\ \frac{1}{4},\frac{3}{4},\frac{1}{2}$
T	62 $Pnma$	B1	$(0,0,2),(-\frac{1}{2},\frac{1}{2},0),(-\frac{1}{2},-\frac{1}{2},0)$	$(c)\ \frac{3}{8},\frac{1}{4},\frac{1}{4}$	$(c)\ \frac{5}{8},\frac{1}{4},\frac{1}{4}$
		B33	$(0,1,0),(0,0,1),(1,0,0)$	$(c)\ \frac{3}{8}-\delta_1,\frac{1}{4},\frac{1}{2}$	$(c)\ \frac{5}{8}-\delta_2,\frac{1}{4},0$
	57 $Pbcm$	B33	$(1,0,0),(0,1,0),(0,0,1)$	$(d)-\frac{1}{4},\frac{5}{8}-\delta_1,\frac{1}{4}$	$(d)\ \frac{3}{4},\frac{3}{8}-\delta_2,\frac{1}{4}$
		B2	$(0,0,-1),(2,2,0),(1,-1,0)$	$(d)\ 0,\frac{5}{8},\frac{1}{4}$	$(d)\ \frac{1}{2},\frac{3}{8},\frac{1}{4}$
MB	11 $P2_1/m$	B1	$(\frac{1}{2},\frac{1}{2},1),(-\frac{1}{2},\frac{1}{2},0),(-\frac{1}{2},-\frac{1}{2},0)$	$(e)\ \frac{1}{4},\frac{1}{4},0$	$(e)\ \frac{3}{4},\frac{1}{4},\frac{1}{2}$
		B33	$(-\frac{1}{2},\frac{1}{2},0),(0,0,1),(1,0,0)$	$(e)\ \frac{1}{4}-2\delta_1,\frac{1}{4},-\frac{1}{8}-\delta_1$	$(e)\ \frac{3}{4}-2\delta_2,\frac{1}{4},\frac{5}{8}-\delta_2$
		B2	$(1,1,0),(1,-1,0),(0,0,-1)$	$(e)\ \frac{1}{4},\frac{1}{4},0$	$(e)\ \frac{3}{4},\frac{1}{4},\frac{1}{2}$

constants are underestimated by about 3% and 1%, respectively, for NaCl and PbS, when compared to the experimental data of 5.562 Å (Ref. 13) and 5.929 Å.[14] The calculated bulk moduli (32.7 GPa for $B1$-NaCl and 64.3 GPa for $B1$-PbS) agree well with the previous LDA results.[11,12] Our calculations and previous calculations both overestimate the bulk moduli [23.4 GPa for B1-NaCl (Ref. 13) and 52.9 GPa for $B1$-PbS (Ref. 14)] by about 10 GPa. A similar level of agreement is also found in the high-pressure phases of NaCl and PbS studied here.

We first calculated the pressures at which the phase transitions occur. This is simply the pressure at which the enthalpy $H = E + PV$ of the initial and final phases are equal. For the $B1$-$B2$ transition in NaCl, we obtained 24.4 GPa, in relatively good agreement with the experimentally determined value[13] of 30 GPa. For the $B1$-$B33$ and $B33$-$B2$ transitions in PbS, we obtained 4.7 and 22.4 GPa, respectively, in relatively good agreement with the experimentally determined values[8] of 2.3 and 22.5 GPa.

To calculate energy/enthalpy barriers along one particular transformation pathway, we first choose one internal coordinate as our transformation coordinate and sample a finite set of its values with the range from the value at the initial phase to the value at the final phase. Other internal coordinates are optimized with the respect to the chosen transformation coordinate using a "bow function method"[15] we recently developed. After the internal coordinates are determined, the external lattice parameters are optimized with the constraints of crystal symmetry and fixed volume. The calculations are then repeated over a finite set of volumes, and the enthalpies ($H = E + PV$) are calculated after the energy vs volume curves are fitted using the finite Eulerian strain equation of state.[16]

The results of our calculations are shown in Figs. 4 and 5 for PbS and NaCl, respectively. In PbS (Fig. 4), the energy barriers for the $B1$-$B33$ and $B33$-$B2$ transitions are calculated at 4.7 and 22.4 GPa, respectively, since these two transitions occur at different pressures. We see that the barriers are approximately equal for the T and MB pathways. The W pathway between $B1$ and $B2$ in PbS occurs at a pressure

higher than 4.7 GPa, so it would not occur at all, and we do not plot its energy barrier.

In NaCl (Fig. 5), $B33$ is a metastable state, so the transition takes place from $B1$ to $B2$ at a single pressure. As in PbS, we see that the energy barriers in NaCl are approximately equal for the T and MB pathways. The barrier for the W pathway, on the other hand, is somewhat higher, suggesting that the T and MB pathways are energetically favored over the W pathway.

We further repeated our calculations with FIREBALL,[17] a first principles tight-binding method based on DFT. As expected, both FIREBALL and VASP predict similar barrier heights even when the two methods calculated different transition pressures. This result shows that our predicted trends of the transition mechanism are not sensitive to any *ab initio* method adopted.

Our energy-barrier calculations do not help us decide which of the two proposed pathways, T and MB, would be
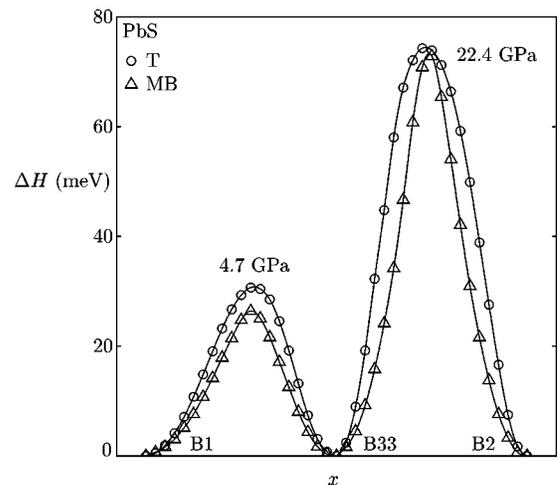

FIG. 4. Relative enthalpy ΔH per Pb-S pair in PbS along the Tolédano (T) and modified Buerger (MB) pathways as a function of the transformation coordinate x, which in this case, is the z displacement of the Na atoms.

FIG. 5. Relative enthalpy ΔH per Na-Cl pair in NaCl along the Watanabe (W), Tolédano (T), and modified Buerger (MB) pathways as a function of the transformation coordinate x, which in this case, is the z displacement of the Na atoms.
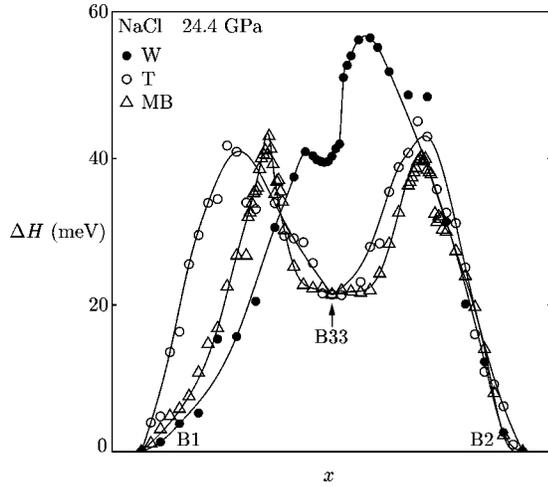
most favorable in the phase transition, either in PbS or in NaCl.

IV. RELATIVE ORIENTATIONS OF *B*1 AND *B*2

In a number of x-ray and neutron diffraction studies[18–22] of various alkali halides, certain orientations in the *B*1 and *B*2 phases were found to be parallel. The earlier studies[18,19] found that
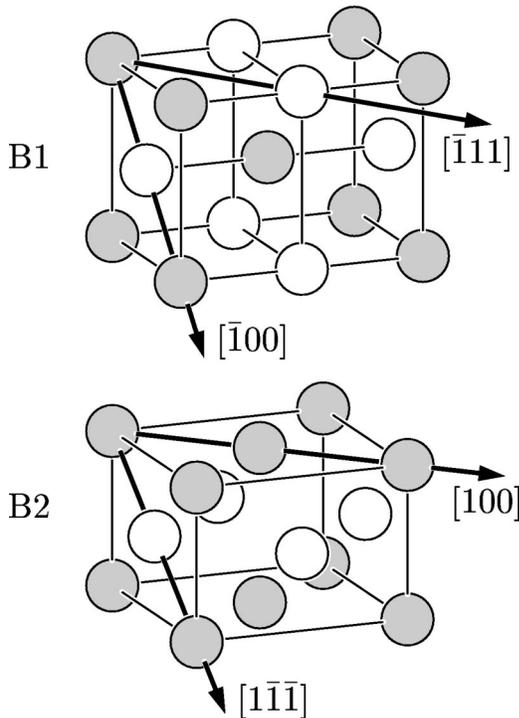

FIG. 6. Possible way in which Eqs. (3) and (4) may be satisfied for the W pathway. The orthorhombic unit cell of *Pmmn* is oriented the same way as in Fig. 1, but from a slightly different view point.
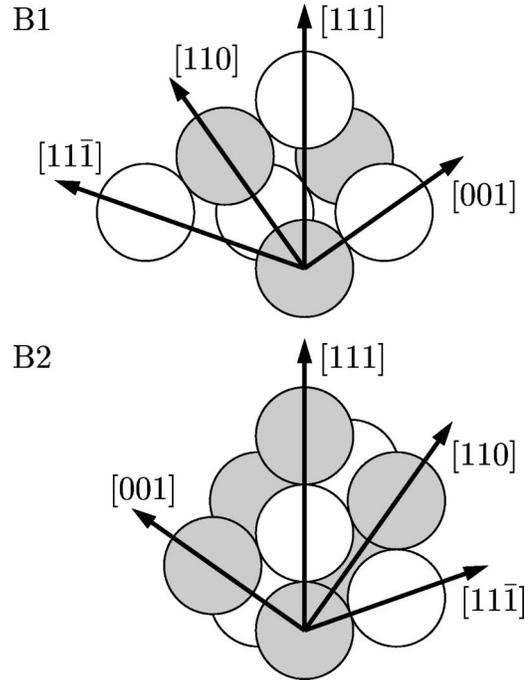

FIG. 7. Possible way in which Eqs. (1) through (4) may be satisfied for the MB pathway. In both structures, the atoms shown lie in the $(1\bar{1}0)$ cubic plane, as in Fig. 1.

$$[001]_{B1}||[110]_{B2} \tag{1}$$

and

$$[110]_{B1}||[001]_{B2}. \tag{2}$$

Here the notation means that the [001] direction in *B*1 is parallel to the [110] direction in *B*2, etc. Later studies[20–22] found that

$$[100]_{B1}||[111]_{B2} \tag{3}$$

and

$$[111]_{B1}||[100]_{B2}. \tag{4}$$

[Note that Eqs. (3) and (4) imply that $[\bar{2}11]_{B1}||[011]_{B2}$ which is the orientation Onodera *et al.*[22] report instead of Eq. (3).] For convenience, let *R*1 denote the relations in Eqs. (1) and (2), and let *R*2 denote the relations in Eqs. (3) and (4). The differences between *R*1 and *R*2 are usually attributed to different external conditions, sample size, etc.

We find that it is actually possible for *R*1 and *R*2 to be satisfied for all three (W,T,MB) pathways. In the analysis of these orientation relations, we must realize that since these relations come from x-ray and neutron diffraction studies, $[111]_{B1}||[100]_{B2}$ actually means that the (111) planes of atoms in *B*1 are parallel to the (100) planes of atoms in *B*2. Furthermore, this statement does not imply that the (111) planes in *B*1 contain the *same atoms* as the (100) planes in *B*2.

With this in mind, we wrote a simple computer program which searched for ways in which *R*1 and *R*2 could be satisfied for each pathway. As will be seen below, we found that

generally $R1$ and $R2$ could only be satisfied if we allowed the crystal to rotate during the phase transition. We chose the results with the smallest angle of rotation.

Let us first consider the W and T pathways. (Since the relative orientation of $B1$ and $B2$ are identical for the W and T pathways, we consider them together.) $R1$ is easily satisfied, as can be seen by inspection in Fig. 1. No rotation of the crystal is required. The orthorhombic axes of $Pmmn$ in $B2$ are parallel to those in $B1$.

$R2$ is a more difficult case. In Fig. 6, we show the best possible way that $R2$ can be satisfied for the W and T pathways. The $[\bar{1}00]_{B1}$ and $[1\bar{1}\bar{1}]_{B2}$ directions pass through the same set of atoms, but those two directions are not the same with respect to the orthorhombic axes. (The face of the unit cell containing $[\bar{1}00]$ in $B1$ is a square, while the face of the unit cell containing $[1\bar{1}\bar{1}]$ in $B2$ is a rectangle. The diagonal of a square is not along the same direction as a diagonal of a rectangle.) Thus, in order for $[\bar{1}00]_{B1}$ to be parallel to $[1\bar{1}\bar{1}]_{B2}$, we must rotate $B2$ with respect to the orthorhombic axes.

In Fig. 6, we see that the $[\bar{1}11]_{B1}$ and $[100]_{B2}$ directions do not even pass through the same set of atoms. However, we must remember that $R1$ and $R2$ do not actually require that. We only require that after the transition, certain directions in $B2$ are parallel to certain directions in $B1$ before the transition. The angle between $[\bar{1}00]_{B1}$ and $[\bar{1}11]_{B1}$ is exactly equal to the angle between $[1\bar{1}\bar{1}]_{B2}$ and $[100]_{B2}$, so we can satisfy $R2$ by rotating $B2$ with respect to the orthorhombic axes. We found the angle of rotation to be about 18°.

Note that rotating $B2$ to satisfy $R2$ means that $R1$ is no longer satisfied. $R1$ cannot be satisfied at the same time as $R2$ is satisfied. Indeed, they were observed in different samples under different experimental conditions.

In the MB pathway, the crystal, as it evolves from $B1$ to $B2$, contracts along the $[111]_{B1}$ direction and expands along directions perpendicular to $[111]_{B1}$. In Fig. 7, we show $B1$ and $B2$ oriented with a common $[111]$ axis. All of the vectors shown in the figure lie in the same $(1\bar{1}0)$ plane. We see from the figure how $R1$ may be satisfied. The crystal needs only to rotate counter clockwise by about 19° during the phase transition. Similarly, $R2$ may be satisfied by rotating the crystal clockwise by about 16° so that $[001]_{B1}\|[11\bar{1}]_{B2}$ and $[11\bar{1}]_{B1}\|[001]_{B2}$. In either case, the rotation causes $[111]_{B1}$ to be not parallel to $[111]_{B2}$.

It is not clear what mechanisms may be present which cause the crystal to rotate during the phase transition. Large strains are present and, especially if there are many domains, it is reasonable to expect some rotation. It is also reasonable to expect different samples under different experimental conditions to rotate differently.

Our analysis shows that the experimentally obtained relations in $R1$ and $R2$ do not definitively favor one of the proposed pathways over another. The W pathway does not require any rotation to satisfy $R1$, but we cannot ignore $R2$ for which the W pathway requires an 18° rotation.

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