Supporting Information

Phase Transformation and Interface Crystallography between TiO_2 and Different Ti_nO_{2n-1} Phases

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Supplementary Figures and Tables

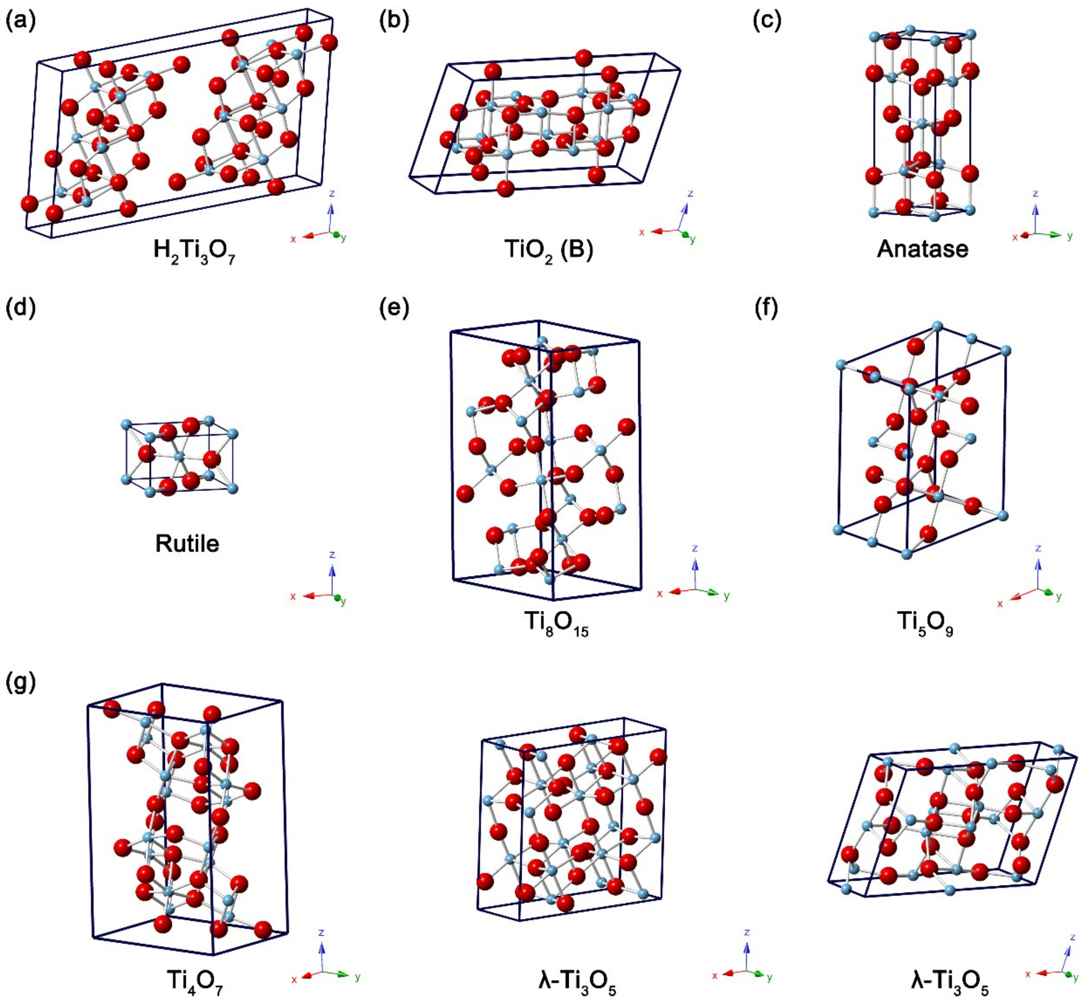

Figure S1 The schematic crystal structures of all the titanium oxide and related phases involved in this work.

Table S1 Space groups and lattice parameters of involved titanium oxides and related phases

Phase	Space Group	Lattice Parameters
$H_2Ti_3O_7$	$C12/m1$	a=16.023 Å, b=3.749 Å, c=9.19 Å, β=101.57°, α=γ=90°
TiO_2 (B)	$C12/m1$	a=12.208 Å, b=3.749 Å, c=6.535 Å, β=107.36°, α=γ=90°
Anatase	$I4_1/amd$	a=b=3.785 Å, c=9.515 Å, α=β=γ=90°
Rutile	$P4_2/mnm$	a=b=4.592 Å, c=2.957 Å, α=β=γ=90°
Ti_8O_{15}	P-1	a=5.53 Å, b=7.134 Å, c=13.401 Å, α=100.54°, β=96.57°, γ=108.51°
Ti_5O_9	$P1$	a=5.60 Å, b=7.120 Å, c=8.870 Å, α=97.60°, β=112.30°, γ=108.50°
Ti_4O_7	A-1	a=5.594 Å, b=7.122 Å, c=12.460 Å, α=95.05°, β=95.19°, γ=108.76°
λ-Ti_3O_5	$C12/m1$	a=9.752 Å, b=3.802 Å, c=9.442 Å, β=91.92°, α=γ=90°
γ-Ti_3O_5	$I12/c1$	a=9.969 Å, b=5.074 Å, c=7.182 Å, β=109.863°, α=γ=90°

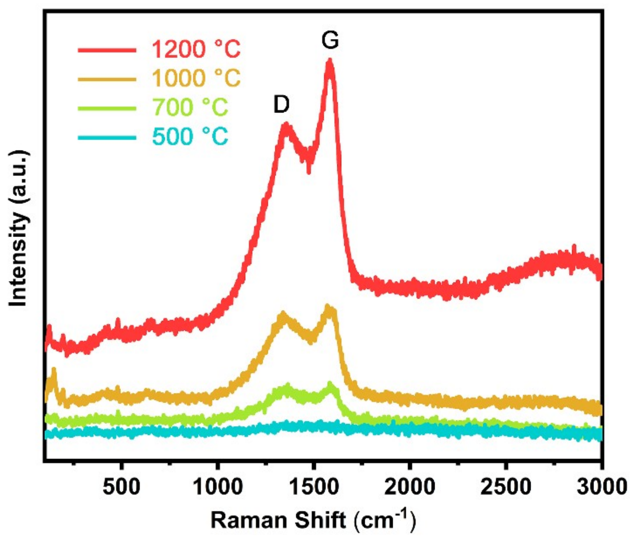

Figure S2 Raman spectroscopy of PDA@$H_2Ti_3O_7$ nanofiber precursor calcinated under different temperatures for 1 hour.

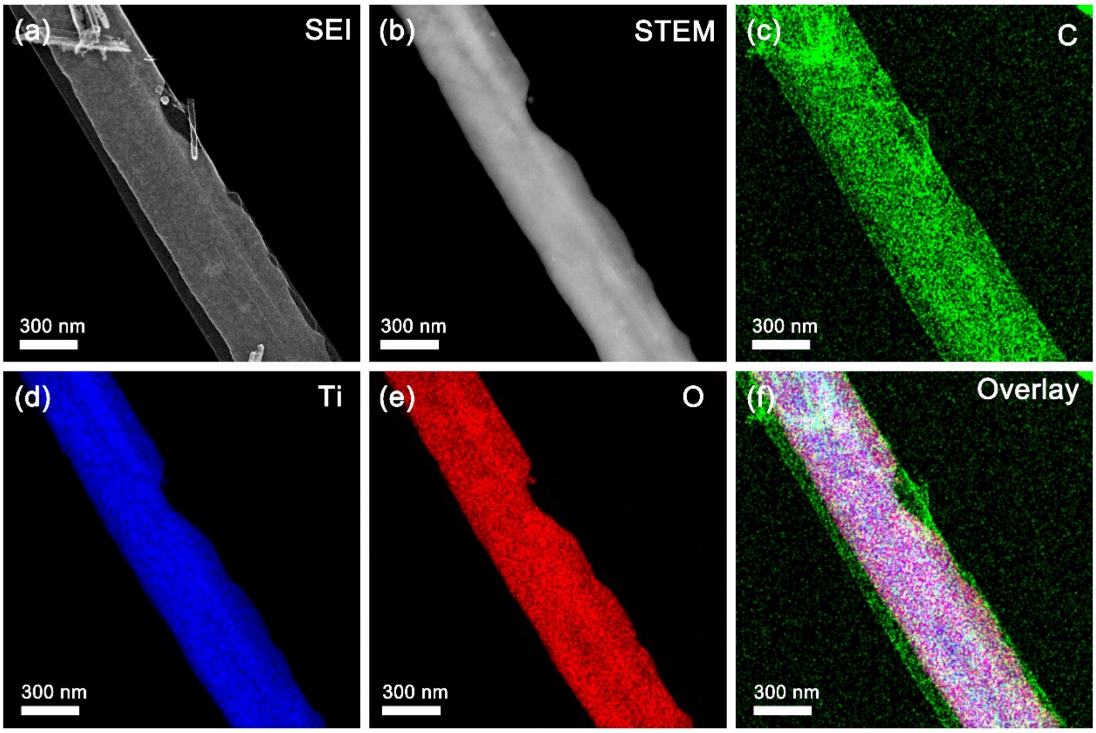

Figure S3 The STEM and corresponding EDX mapping characterization results of the PDA@$H_2Ti_3O_7$ precursor calcinated at 1000 °C: (a) Second Electron Image (SEI); (b) STEM-DF image; (c-e) Elemental mapping signal for C, Ti and O; (f) Overlay elemental mapping of the above 3 elements.

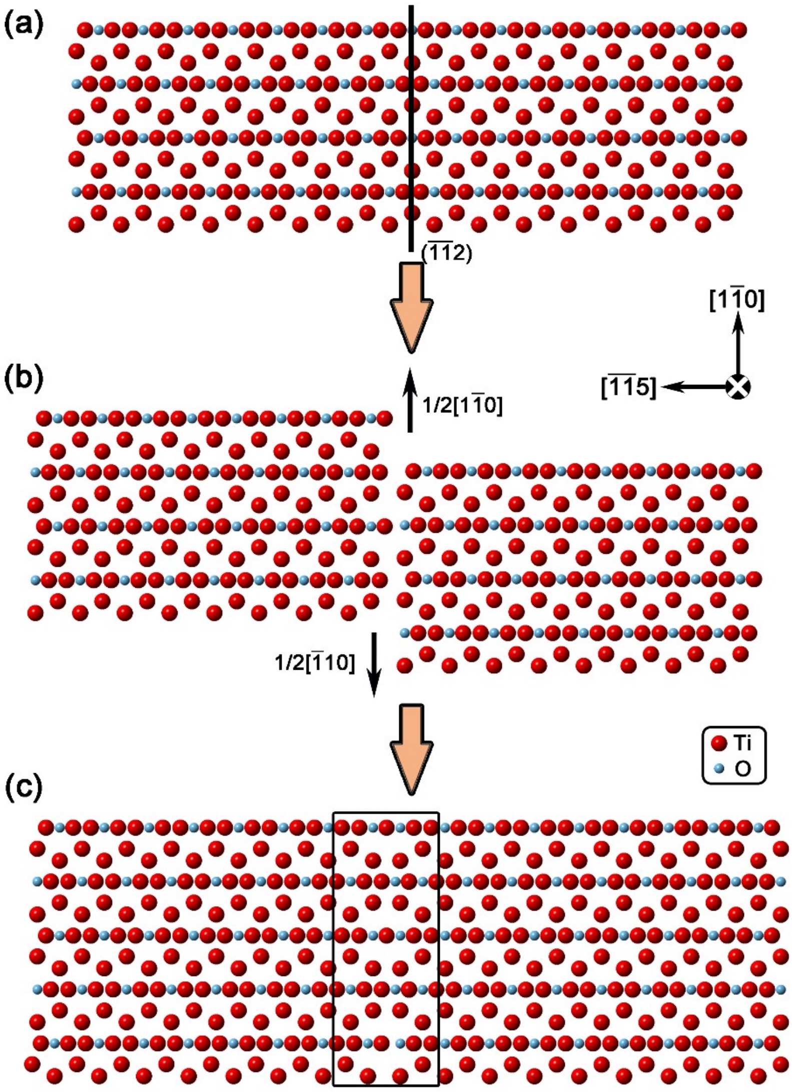

Figure S4 The schematic illustration of the formation process of the sheared structure in rutile.

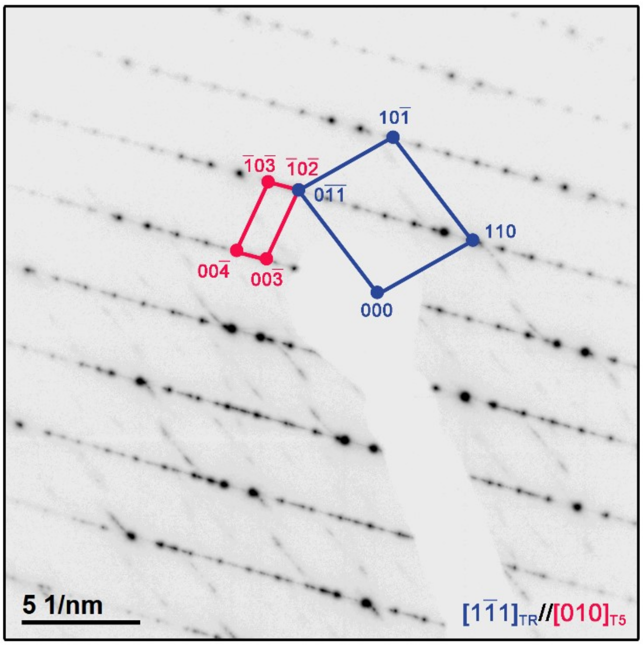

Figure S5 The SAED patterns of TR/T5 dual phase nanofibers

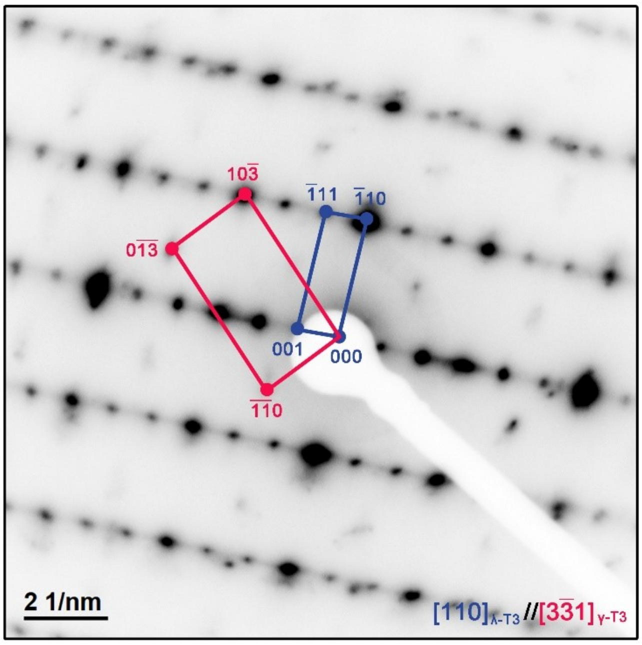

Figure S6 The SAED patterns of λ-T3/γ-T3 dual phase nanofibers

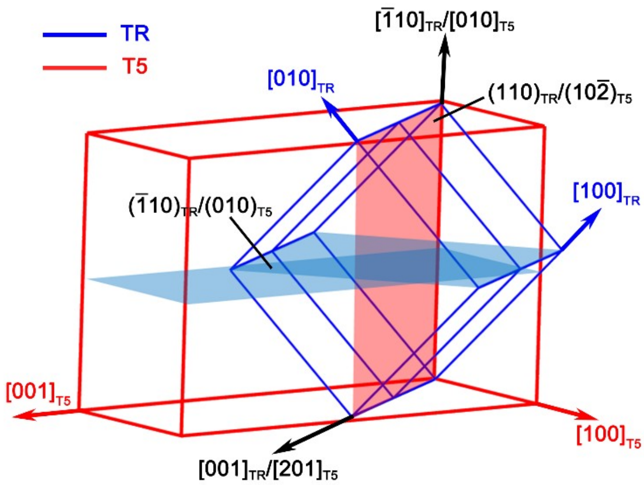

Figure S7 The Bain orientation relationships between TR and T5 phase

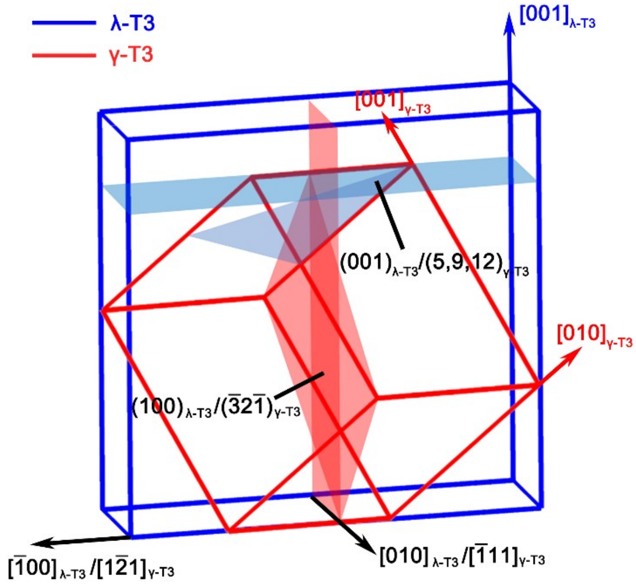

Figure S8 The Bain orientation relationships between λ-T3 and γ-T3 phase

The detailed invariant line strain calculation process

As mentioned in the main text, the rotation axis $\boldsymbol{u}$ and angle θ when using Euler's equation for rigid-body rotation can be determined as follows:

$$\frac{(P_2 - P_1) \times (Q_2 - Q_1)}{(P_2 + P_1) \cdot (Q_2 - Q_1)} = u\left[tan^{\theta}/_{2}\right] \tag{S-1}$$

Here, $\mathbf{P_1}$ and $\mathbf{Q_1}$ are the invariant unit vector in real and in reciprocal space, $\mathbf{P_2}$ and $\mathbf{Q_2}$ are the corresponding invariant unit vector after the Bain deformation. Considering the initial lattice correspondence of TR/T5 and λ-T3/γ-T3 phase transformation systems,

$[001]_{TR}//[201]_{T5}$ and $[010]_{\lambda-T3}//[11\bar{1}]_{\gamma-T3}$ are selected as the rotation axes. Therefore, $\mathbf{P_1}$ can be chosen as $[001]_{TR}$ and $[010]_{\lambda-T3}$ respectively. Under this condition, $[001]_{TR}$ and $[010]_{\lambda-T3}$ are identical to $[010]$ in the reference coordination system for TR/T5 and λ-T3/γ-T3 phase transformation systems. That is,

$$P_1 = [010],\ P_2 = B \cdot P_1 = [0,\eta_2,0] \tag{S-2}$$

According to the Invariant Deformation Element model, $\mathbf{Q_1}$ must be perpendicular to $\mathbf{P_1}$. The following equations can be obtained:

$$Q_1 = [h0l],\ Q_2 = B^{-1} \cdot Q_1 = \left[\frac{h}{\eta_1},0,\frac{l}{\eta_3}\right] \tag{S-3}$$

When applying $|Q_1| = |Q_2|$, the relational expressions between *k* and *l* can be obtained:

$$h^2 + l^2 = \frac{h^2}{\eta_1^2} + \frac{l^2}{\eta_3^2} \tag{S-4}$$

Considering the 2 phase transformation systems, the values of *h* and *l* can be calculated separately. Furthermore, Q_1, $\boldsymbol{u}$ and θ can also be calculated accordingly. Table S1 summarized the calculated results of the above parameters.

Table S1 The Bain strain matrix and several calculated parameters in TR/T5 and λ-T3/γ-T3 phase transformation systems

Phase Transformation System	Bain Strain Matrix	h	Q_1	$\boldsymbol{u}$	θ
TR/T5	$\begin{pmatrix} 1.2462 & 0 & 0 \\ 0 & 0.9586 & 0 \\ 0 & 0 & 0.9956 \end{pmatrix}$	$0.1577l$	[0.1577, 0, 1]	$[010] = [001]_{TR}$	-1.78°
λ-T3/γ-T3	$\begin{pmatrix} 1.0939 & 0 & 0 \\ 0 & 0.9905 & 0 \\ 0 & 0 & 0.9704 \end{pmatrix}$	$0.6139l$	[0.6139, 0, 1]	$[010] = [010]_{\lambda-T3}$	2.97°

Then the total strain matrix $\boldsymbol{A}$ can be written as:

$$A = RB = \begin{pmatrix} cos\theta & 0 & sin\theta \\ 0 & 1 & 0 \\ -sin\theta & 0 & cos\theta \end{pmatrix} \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} \tag{S-5}$$

Let $(A - I)X = 0$, then we can obtain:

$$|A-I| = \left|\begin{pmatrix} cos\theta & 0 & sin\theta \\ 0 & 1 & 0 \\ -sin\theta & 0 & cos\theta \end{pmatrix}\begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} - \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\right| = (\eta_2 - 1)[1 + \eta_1\eta_3 - (\eta_1 = 0$$

(S-6)

The rotation angle θ can be obtained as:

$$cos\theta = \frac{1+\eta_1\eta_3}{\eta_1+\eta_3} \qquad \text{(S-7)}$$

In order to calculate the eigenvalue λ_i of the lattice deformation matrix, we let $|(A-\lambda I)| = 0$, then:

$$|A-\lambda I| = \left|\begin{pmatrix} cos\theta & 0 & sin\theta \\ 0 & 1 & 0 \\ -sin\theta & 0 & cos\theta \end{pmatrix}\begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} - \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{pmatrix}\right| = (\lambda - 1)(\lambda - \eta_1\eta_3)(\eta_2 - \lambda = 0$$

(S-8)

Therefore, the three eigenvalues are determined to be $\lambda_1 = 1$, $\lambda_2 = \eta_1\eta_3$, $\lambda_3 = \eta_2$. Obviously, one of the eigenvalues always equals to 1. Hence, eigenvectors Vi of the matrix $\boldsymbol{A}$ can be calculated by letting $\boldsymbol{AX} = \lambda\boldsymbol{X}$, then:

$$(A-\lambda I)X = \left[\begin{pmatrix} cos\theta & 0 & sin\theta \\ 0 & 1 & 0 \\ -sin\theta & 0 & cos\theta \end{pmatrix}\begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix} - \begin{pmatrix} \lambda & 0 & 0 \\ 0 & \lambda & 0 \\ 0 & 0 & \lambda \end{pmatrix}\right]\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} (\eta_1 cos\theta - \lambda)X + \\ (\eta_2 - \lambda) \\ (-\eta_1 sin\theta)X + (\eta_3 \end{pmatrix} = 0$$

(S-9)

After putting the calculated eigenvalues and rotation angles θ into (S-9), then we can obtain:

(1) If $\lambda_1 = 1$, then Y=0, and $\frac{X}{Z} = \frac{-\eta_3 sin\theta}{\eta_1 cos\theta - 1} = \frac{\eta_3 cos\theta - 1}{\eta_1 sin\theta} = \sqrt{\frac{1-\eta_3^2}{\eta_1^2 - 1}}$. Therefore,

$V_1 = \left[1,0,\sqrt{\frac{1-\eta_3^2}{\eta_1^2-1}}\right]$.

(2) If $\lambda_2 = \eta_1\eta_3$, then Y=0, and $\frac{X}{Z} = \frac{-\eta_3 sin\theta}{\eta_1 cos\theta - \eta_1\eta_3} = \frac{\eta_3 cos\theta - \eta_1\eta_3}{\eta_1 sin\theta} = \frac{\eta_3}{\eta_1}\sqrt{\frac{\eta_1^2 - 1}{1 - \eta_3^2}}$.

Therefore, $V_2 = \left[1,0,\frac{\eta_3}{\eta_1}\sqrt{\frac{\eta_1^2 - 1}{1 - \eta_3^2}}\right]$.

(3) If $\lambda_3 = \eta_2$, then Y can be assigned to any real number, and X=Z=0, $V_3 = [010]$.

The eigenplanes determined by the three eigenvectors are:

$$F_1 = \begin{vmatrix} i & j & k \\ 1 & 0 & \sqrt{\frac{1-\eta_3^2}{\eta_1^2 - 1}} \\ 1 & 0 & \frac{\eta_3}{\eta_1}\sqrt{\frac{\eta_1^2 - 1}{1 - \eta_3^2}} \end{vmatrix} = \left(0,\frac{\eta_3}{\eta_1}\sqrt{\frac{\eta_1^2 - 1}{1 - \eta_3^2}} - \sqrt{\frac{1-\eta_3^2}{\eta_1^2 - 1}},0\right) \tag{S-10}$$

$$F_2 = \begin{vmatrix} i & j & k \\ 1 & 0 & \sqrt{\frac{1-\eta_3^2}{\eta_1^2 - 1}} \\ 0 & 1 & 0 \end{vmatrix} = \left(-\sqrt{\frac{1-\eta_3^2}{\eta_1^2 - 1}},0,1\right) \tag{S-11}$$

$$F_3 = \begin{vmatrix} i & j & k \\ 1 & 0 & \frac{\eta_3}{\eta_1}\sqrt{\frac{\eta_1^2 - 1}{1 - \eta_3^2}} \\ 0 & 1 & 0 \end{vmatrix} = \left(-\frac{\eta_3}{\eta_1}\sqrt{\frac{\eta_1^2 - 1}{1 - \eta_3^2}},0,1\right) \tag{S-12}$$