## First-principles study of charged steps on $180^{\circ}$ domain walls in ferroelectric $\mathrm{PbTiO}_{3}$

Y. X. Jiang, , Y. J. Wang, , D. Chen, , Y. L. Zhu, and , and X. L. Ma

Citation: Journal of Applied Physics 122, 054101 (2017); doi: 10.1063/1.4997461
View online: http://dx.doi.org/10.1063/1.4997461
View Table of Contents: http://aip.scitation.org/toc/jap/122/5
Published by the American Institute of Physics

## Articles you may be interested in

Effect of shear stress in ferroelectric solid solutions with coexisting phases Journal of Applied Physics 122, 054102 (2017); 10.1063/1.4994171

Periodic arrays of flux-closure domains in ferroelectric thin films with oxide electrodes
Applied Physics Letters 111, 052901 (2017); 10.1063/1.4996232
Domain structures in circular ferroelectric nano-islands with charged defects: A Monte Carlo simulation Journal of Applied Physics 122, 044103 (2017); 10.1063/1.4996350

Electrical conduction at domain walls in lead titanate $\left(\mathrm{PbTiO}_{3}\right)$ single crystals
Applied Physics Letters 110, 213108 (2017); 10.1063/1.4983642
$\mathrm{BaTiO}_{3} / \mathrm{SrTiO}_{3}$ heterostructures for ferroelectric field effect transistors
Applied Physics Letters 110, 232902 (2017); 10.1063/1.4985014
Ferroelectric, elastic, piezoelectric, and dielectric properties of $\mathrm{Ba}\left(\mathrm{Ti}_{0.7} \mathrm{Zr}_{0.3}\right) \mathrm{O}_{3}-\mathrm{x}\left(\mathrm{Ba}_{0.82} \mathrm{Ca}_{0.18}\right) \mathrm{TiO}_{3} \mathrm{~Pb}$-free ceramics
Journal of Applied Physics 122, 044105 (2017); 10.1063/1.4996353

## AIP <br> Journal of Applied Physics

Save your money for your research. It's now FREE to publish with us no page, color or publication charges apply.

# First-principles study of charged steps on $180^{\circ}$ domain walls in ferroelectric $\mathrm{PbTiO}_{3}$ 

Y. X. Jiang, ${ }^{1}$ Y. J. Wang, ${ }^{1}$ D. Chen, ${ }^{1, a)}$ Y. L. Zhu, ${ }^{1}$ and X. L. Ma ${ }^{1,2, a)}$<br>${ }^{1}$ Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Wenhua Road 72, 110016 Shenyang, China<br>${ }^{2}$ School of Materials Science and Engineering, Lanzhou University of Technology, Langongping Road 287, 730050 Lanzhou, China

(Received 20 April 2017; accepted 22 July 2017; published online 4 August 2017)


#### Abstract

The atomic-scale mechanism of domain wall motion in ferroelectrics is commonly accepted to be nucleation and the movement of steps on the domain walls. Although very important in understanding the mechanism of domain wall motion and domain switching, the detailed atomic structures of steps have nevertheless been scarcely explored. In this work, the charged steps of these structures on $180^{\circ}$ domain walls in $\mathrm{PbTiO}_{3}$ were investigated using first-principles computations. Contrary to the previous understanding that there is a sudden jump at a step from one atomic plane to an adjacent plane, our computation results suggest that it is actually a gradual transition and the actual steps lie at atomic planes with the approximate Miller indices ( $30 \overline{1}$ ). A large polarization rotation was found around the steps, making the polarization distribution Ising-Néel-like. The barriers for the motion of steps along domain walls were found to be much lower than those for which the domain wall is moving as a whole. These findings provide valuable information for further investigations of the domain switching mechanism at the atomic scale. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4997461]


## I. INTRODUCTION

Ferroelectric perovskites including $\mathrm{BaTiO}_{3}, \mathrm{PbTiO}_{3}$, and $\mathrm{Pb}\left(\mathrm{Zr}_{\mathrm{x}}, \mathrm{Ti}_{1-\mathrm{x}}\right) \mathrm{O}_{3}$, have been widely studied in recent years because of their fascinating potential application in many ferroelectric devices, such as ferroelectric random access memories. ${ }^{1,2}$ It is known that the switching mechanism of the ferroelectric polarization, which essentially determines the performance of ferroelectric devices, is based on the movement of ferroelectric domain walls (DWs). ${ }^{3-6}$ Steps on the DWs play an important role in the mechanism underlying the DW motion with several switching models being proposed. ${ }^{7-9}$ Miller and Weinreich ${ }^{7}$ suggested that the motion of $180^{\circ}$ DWs in $\mathrm{BaTiO}_{3}$ results from the repeated nucleation along existing parent DWs of triangular steps of one lattice-constant thickness. With no consideration of the atomic-scale structure of the steps, however, the sharp steps of this model result in nucleation energies much higher than the experimental results. ${ }^{10}$ Recently, Shin et al. ${ }^{8}$ demonstrated that a model with diffused steps does effectively decrease the nucleation energy yielding better agreement with experimental results than sharp steps. ${ }^{8,9}$

An atomic-scale analysis of steps would be beneficial in exploring further the switching mechanism of ferroelectrics as currently there are very few results regarding experimental and theoretical aspects. Using the aberration-corrected transmission electron microscope, Jia et al. ${ }^{11}$ observed charged steps on (110)-oriented $180^{\circ}$ DWs in $\mathrm{Pb}\left(\mathrm{Zr}_{0.2} \mathrm{Ti}_{0.8}\right) \mathrm{O}_{3}$ (PZT) but the step structure had not been detailed. Recently, De

[^0]Luca et al. ${ }^{12}$ reported a mixed Ising-Néel-type rotation of polarization across inclined $180^{\circ}$ DWs in PZT, although the role of charged steps on inclined $180^{\circ}$ DWs was not directly addressed. From a theoretical perspective, Angoshtari and Yavari ${ }^{13}$ described anharmonic lattice static simulations of neutral steps on (100)-oriented $180^{\circ} \mathrm{DWs}$ in $\mathrm{PbTiO}_{3}$ (PTO), comparing results with those with no charged steps. Indeed, charged steps are not stable in the remnant state because of a depolarization field induced by bound charges at the steps. However, charged steps are commonly observed in improper ferroelectric systems ${ }^{14}$ because the electric polarization is subordinate to some higher level order parameters. Therefore, the induced depolarization field in typical ferroelectrics may play a more important role in stabilizing the polarization than in improper ferroelectrics.

As is well known, first-principles computation is one effective method for atomic-scale studies. The atomic structures, polarization characters, and energies of various DWs in many ferroelectric perovskites have been well scrutinized using this method. ${ }^{15-22}$ With few first-principles studies on charged steps on ferroelectric DWs, we undertake in this work first-principles computations to investigate charged steps in tetragonal PTO. There are two types of DWs in PTO, namely, $180^{\circ}$ and $90^{\circ}$ DWs. The former can be regarded as a boundary between two domains with oppositely oriented polarizations; the charged step on this boundary is our main topic of interest. We provide not only detailed atomic structures of the charged steps, but also give the barriers for the step motion. These results may shed light on understanding of the atomic-scale mechanism underlying polarization switching.

## II. CALCULATION METHODS

Our density functional theory (DFT) calculations ${ }^{23}$ were performed using the local density approximation ${ }^{24}$ with the projector-augmented-wave method ${ }^{25,26}$ in the Vienna $a b$ initio simulation package. ${ }^{27,28}$ The valence electrons are assumed to be $\mathrm{Pb} 5 d^{10} 6 s^{2} 6 p^{2}$, Ti $3 s^{2} 3 p^{6} 3 d^{2} 4 s^{2}$, and $\mathrm{O} 2 s^{2} 2 p^{4}$ in the isolated atom form. An energy cutoff of 500 eV and a Gaussian smearing of 0.1 eV were used for all computations. The conjugate-gradient method was used for the structural optimization; convergence was deemed satisfied when all Hellmann-Feynman forces were less than $10 \mathrm{meV} / \AA$.

The fully relaxed structure of the bulk PTO tetragonal phase $(P 4 \mathrm{~mm})$ with $a_{0}=3.867 \AA$ and $c_{0} / a_{0}=1.043$ was applied in all the following supercells. In our DFT calculations, a series of $X \times 1 \times Z$ supercells $(X=8,10,12,14$, and 16 and $Z=2,4,6,8$, and 10) were configured for the one-lat-tice-constant-thick charged steps on the (100)-oriented $180^{\circ}$ DWs. Brillouin-zone integrations were performed with $6 \times 6 \times 6,1 \times 6 \times 3$ and $1 \times 6 \times 1$ Monkhorst-Pack k-point meshes ${ }^{29}$ for the bulk, the $X \times 1 \times 2$ supercells, and the $X \times 1 \times Z$ supercells $(Z=4,6,8$, and 10$)$, respectively. The initial structures of the steps in the $10 \times 1 \times 4$ supercell are depicted (Fig. 1). The basis vectors of the supercell are along the $\left[\begin{array}{lll}1 & 0 & 0\end{array}\right],\left[\begin{array}{lll}0 & 1 & 0\end{array}\right]$, and $\left[\begin{array}{lll}1 & 0 & 4\end{array}\right]$ directions, respectively. Similar to previous studies, ${ }^{15,16}$ we chose the PbO atomic planes as DWs (blue lines in Fig. 1). The PbO-centered (10 0) $180^{\circ}$ DWs were demonstrated to be the most stable. ${ }^{16} \mathrm{We}$ considered two step planes, that for PbO and for $\mathrm{TiO}_{2}$ (red lines). The models for both planes were further classified as head-to-head (h-) and tail-to-tail (t-) according to the configurations of local polarizations across the steps (black


FIG. 1. $10 \times 1 \times 4$ supercells of (a) the $\mathrm{PbO}(001)$ steps and (b) $\mathrm{TiO}_{2}(001)$ steps on the $\mathrm{PbO}\left(\begin{array}{lll}1 & 0 & 0\end{array}\right)$ DWs. The blue and red lines, and black arrows indicate $\left(\begin{array}{lll}1 & 0 & 0\end{array}\right)$ DWs, ( 00101$)$ steps, and polarization directions, respectively.
arrows). The four step models that arise are labeled $\mathrm{h}-\mathrm{PbO}$, $\mathrm{h}-\mathrm{TiO}_{2}, \mathrm{t}-\mathrm{PbO}$, and $\mathrm{t}-\mathrm{TiO}_{2}$.

To distinguish the polarization distribution clearly, we introduced indices $i$ and $j$ to mark the unit cells along the [1000] and [0010 $\left.\begin{array}{ll}1 & 1\end{array}\right]$ directions (Fig. 1). The polarization of the unit cell $i j$ was calculated using

$$
\begin{equation*}
\mathbf{P}^{i j}=\frac{e}{\Omega_{\mathrm{c}}} \sum w_{\alpha} Z_{\alpha}^{*} u_{\alpha}^{i j} \tag{1}
\end{equation*}
$$

where $e, \Omega_{\mathrm{c}}, w_{\alpha}, Z_{\alpha}{ }^{*}$, and $\mathbf{u}_{\alpha}{ }^{i j}$ denote, respectively, the electron charge, the volume of a unit cell, the weight factor, the Born effective charge, and the relative displacement from the centrosymmetric position of the $\alpha$ ion $(\mathrm{Pb}, \mathrm{Ti}$, or O$)$ in the unit cell $i j$. For the supercells containing PbO and $\mathrm{TiO}_{2}$ steps, two types of unit cells (Ti-centered and O-centered) are adopted to calculate the polarizations.

## III. RESULTS AND DISCUSSION

## A. Extension of steps normal to DW planes

The distributions of $P_{x}{ }^{i j}$ and $P_{z}{ }^{i j}$-the polarization components along [ $\left.\begin{array}{lll}1 & 0 & 0\end{array}\right]$ and [ $\left.\begin{array}{lll}0 & 1\end{array}\right]$-in a series of $X \times 1 \times 4$ supercells $(X=8,10,12,14$, and 16) were analyzed to determine the appropriate value of $X$ that successfully describes the polarization distributions around the steps. From the distributions of $P_{x}{ }^{i j}$ and $P_{z}{ }^{i j}$ for $j=2$ in the $X \times 1 \times 4$ supercells with the $\mathrm{PbO}\left(\begin{array}{ll}0 & 0\end{array}\right)$ step model [Fig. 2(a)], we find that the magnitude of $P_{z}{ }^{i j}$ converges to $83 \mu \mathrm{C} / \mathrm{cm}^{2}$, the value in the bulk, as the distance from the DWs increases to about 2 unit cells. This implies that $X=8$ is sufficient to describe the distribution of $P_{z}{ }^{i j}$. As head-to-head and tail-to-tail steps appear in pairs in a single supercell, there should be an electric potential difference between the two steps, ${ }^{34}$ which is why non-zero $P_{x}{ }^{i j}$ components are present there. For unit cells sufficiently far away from the steps, the $P_{x}{ }^{i j}$ components should converge to zero. The $P_{x}^{i j}$ components around the steps are almost the same for the different models, especially for models with $X>10$ [Fig. 2(b)]. However, the magnitude of $P_{x}^{i j}$ away from the steps does not converge to zero, even for the $X=16$ model. In a compromise between precision and computational expense, we chose the $X=12$ models by fixing one half of the models and relaxing the atoms in the other half. The polarization distributions of both $P_{x}{ }^{i j}$ and $P_{z}{ }^{i j}$ around the steps in the locally fixed models are nearly the same as the fully relaxed models, which justified the effectiveness of our locally fixed models. The details are given in Secs. III B and III C.

## B. Extension of steps along DW planes

To determine the extension of the steps along the DW planes, the specific positions of the DWs were determined in a nonlinear fitting. In each step model, we separated the unit cells into several groups according to index $j$. Within each group, we fitted $P_{z}{ }^{i j}$ to the one-dimensional solution of the $180^{\circ}$ DW from the sixth-order Landau-Ginzburg-Devonshire theory ${ }^{30,31}$


$$
\begin{equation*}
P_{z}(x)=P_{z}^{0} \frac{\sinh \left(\frac{x-x_{0}}{\xi}\right)}{\left[\mathrm{A}+\sinh ^{2}\left(\frac{x-x_{0}}{\xi}\right)\right]^{1 / 2}} \tag{2}
\end{equation*}
$$

where $P_{z}{ }^{0}$ and $\xi$ denote the magnitude of polarization in the bulk and the half width of the DW; position $x_{0}$ is where the fitting curve crosses the zero line and is taken as the specific position of the DW. The fitted model has proved to work well in describing the relationship between the polarization distribution and the DW position in many perovskite materials. ${ }^{18,19,30,31}$

Figure 3 shows the fitted results for the h-PbO steps. We systematically changed the supercell size from $12 \times 1 \times 2$ to $12 \times 1 \times 8$. Only the $12 \times 1 \times 8$ supercell successfully describes the step structure-a locally curved DW; otherwise we can only obtain sloping DWs (needed for discussions in Sec. IIIC) in small supercells, such as the $12 \times 1 \times 2$ and $12 \times 1 \times 4$. In the $12 \times 1 \times 8$ supercell, the curved DW distributed over groups $j$ from 2 to 7 , whereas the DW positions still conform to $\mathrm{PbO}\left(\begin{array}{lll}1 & 0 & 0\end{array}\right)$ atomic planes in groups that $j$


FIG. 3. Polarization profiles of the $\mathrm{h}-\mathrm{PbO}$ model in the $12 \times 1 \times 2$ (a), $12 \times 1 \times 4$ (b), $12 \times 1 \times 6$ (c), and $12 \times 1 \times 8$ (d) supercells. The black vectors indicate $P_{z}^{i j}$; the red and blue lines trace the fitted curves and DWs, respectively.
from 1 and 8 ; this means the periodic images of steps have been separated. Similar fitted results were also found in other types of step models. Both the head-to-head steps may be described by $12 \times 1 \times 8$ supercells, whereas we have to use $12 \times 1 \times 10$ supercells to describe the two tail-to-tail steps. Therefore, in the following, the $12 \times 1 \times 10$ supercells were used to study the detailed atomic structures of steps.

Using the fitted results of the four step structures (Fig. 4), the tangent planes for the curved DWs across the centers of the steps were determined (green lines). The values of


FIG. 4. Polarization profiles of the (a) $h-\mathrm{PbO}$, (b) $h-\mathrm{TiO}_{2}$, (c) $t-\mathrm{PbO}$, and (d) $\mathrm{t}-$ $\mathrm{TiO}_{2}$ step models. The results of the $12 \times 1 \times 10$ supercells (only the relaxed areas) are shown. The green lines mark the tangent plane of each step.

TABLE I. Cotangent values of the angle $\alpha$ for the four step models.

| Initial structure | h-PbO | h-TiO | $\mathrm{t}-\mathrm{PbO}$ | $\mathrm{t}-\mathrm{TiO}_{2}$ |
| :--- | :---: | :---: | :---: | :---: |
| $\cot (\alpha)$ | 2.51 | 2.61 | 2.76 | 2.99 |

$\cot (\alpha)$ are listed in Table I, where $\alpha$ denotes the angle between the tangent plane and the (100) DW [Fig. 4(a)]. All the values range from 2.5 to 3 , indicating that the vertical extension of the step is about 3 unit cells. Moreover, the vertical extensions of the tail-to-tail steps are larger than those of the head-to-head steps.

Because all the steps are deflected from their initial (00 1) planes, the designations $h-\mathrm{PbO}, \mathrm{h}-\mathrm{TiO}_{2}, \mathrm{t}-\mathrm{PbO}$, and $\mathrm{t}-\mathrm{TiO}{ }_{2}$ are no longer accurate. The crystallographic planes of the steps must be reassigned (Fig. 5). From the values of $\cot (\alpha)$ in Table I, the crystallographic planes are approximately (30 $\overline{1}$ ) with the atomic configuration of $\mathrm{O}_{2}$ or PbTiO , (red dashed lines in Fig. 5). Hence the step models are relabeled as h- $\mathrm{O}_{2}$ (30 0 ), h-PbTiO (30 $\overline{1}$ ), $\mathrm{t}-\mathrm{O}_{2}(30 \overline{1})$, and $\mathrm{t}-\mathrm{PbTiO}(30 \overline{1})$.

## C. Polarization rotation around steps

Besides the slope characteristics, we also found a significant polarization rotation around the steps. The distributions of $\mathbf{P}^{i j}$ for the four step models are displayed using colorscaled maps (Fig. 6). The angle of $\theta^{i j}$ of $\mathbf{P}^{i j}$ relative to the [0 0 1] direction is calculated from

$$
\begin{equation*}
\theta^{i j}=\arctan \left(\frac{P_{x}^{i j}}{\left|P_{z}^{\mathrm{ij}}\right|}\right) \tag{3}
\end{equation*}
$$

In all four structures, a Néel-like rotation of the polarization emerges around the steps, making the polarization distribution Ising-Néel-like.

The Ising-Néel-like characteristic around the steps emerges locally over a vertical range of $4 c_{0}$. However, De Luca et al. ${ }^{12}$ reported that the entire inclined $180^{\circ} \mathrm{DW}$ in PZT is of Ising-Néel-type. In their work, the $180^{\circ}$ DW is inclined by about $17^{\circ}$, signifying that the averaged vertical
distance between steps on the DW is about $3 c_{0}$. According to our results of Sec. III B, the steps are connected to each other in this case. Therefore the Ising-Néel-like character extends over the entire inclined DW in their work.

The polarization rotation can be further understood using a bound charge analysis. The bound charge is calculated using ${ }^{32}$

$$
\begin{equation*}
\rho^{\text {bound }}=-\nabla \cdot \mathbf{P} \tag{4}
\end{equation*}
$$

which simplifies to $\rho^{\text {bound }}=-\frac{\partial P_{x}}{\partial x}-\frac{\partial P_{z}}{\partial z}$ in this work. Figure 7 shows the bound charge density distributions of the four steps. Each step exhibits a sandwich-like distribution for the bound charges along the [100] direction. For the head-tohead steps [Figs. 7(a) and 7(b)], the major positive charges accumulate at the center $(i=0)$, whereas the minor negative charges accumulate in the two unit cells nearby $(i= \pm 1)$. Taking the $\mathrm{h}-\mathrm{O}_{2}(30 \overline{1})$ model as an example [Fig. 7(a)], the maximum (positive center) and minimum (negative center) charge densities are $2.8 \times 10^{8} \mathrm{C} / \mathrm{m}^{3}$ and $-1.3 \times 10^{8} \mathrm{C} / \mathrm{m}^{3}$, respectively. For the tail-to-tail steps, the distributions of positive and negative charges are just the opposite [Figs. 7(c) and 7(d)]. The presence of bound charges may induce a redistribution of charged species, such as electrons and holes, ${ }^{33,34}$ making the charged steps conductive. It has been reported that, from the flexoelectric effect, Néel-like polarizations are also present around the $\left(\begin{array}{lll}1 & 0 & 0\end{array}\right) 180^{\circ}$ DWs. ${ }^{34}$ The extremum of the induced bound charge density at the Néellike $\left(\begin{array}{ll}1 & 0\end{array}\right) 180^{\circ} \mathrm{DWs}^{35}$ is $1.5 \times 10^{7} \mathrm{C} / \mathrm{m}^{3}$, about one order of magnitude smaller than those at the step centers. Thus, the conductivity of the charged steps should be much larger than that of the Néel-like (100) $180^{\circ}$ DWs.

In addition, we note that the $\mathrm{PbTiO}(30 \overline{1})$ steps have smaller bound charge densities at the step centers than those of $\mathrm{O}_{2}\left(\begin{array}{lll}3 & 0 & \overline{1}\end{array}\right)$; see Table II. Moreover, the $\mathrm{PbTiO}\left(\begin{array}{ll}3 & 0 \\ 1\end{array}\right)$ steps have a smaller angle $\alpha$, and hence longer extensions of the steps along the DW planes than those of $\mathrm{O}_{2}\left(\begin{array}{lll}3 & 0 & \overline{1}\end{array}\right)$. Therefore the bound charges diminish in number as the angle $\alpha$ decreases, in agreement with previous work. ${ }^{33,34}$


FIG. 5. Approximate crystallographic planes of the (a) h- $\mathrm{O}_{2}(30 \overline{1})$, (b) h- $\mathrm{PbTiO}(30 \overline{1})$, (c) $t-\mathrm{O}_{2}(30 \overline{1})$, and (d) $t-\mathrm{PbTiO}$ ( $30 \overline{1}$ ) step models. The black, blue, and red dots mark the positions of atoms $\mathrm{Pb}, \mathrm{Ti}$, and O , respectively, around steps.


FIG. 6. Color-scaled maps of the rotation angles $\theta^{i j}$ around step models (a) $h-\mathrm{O}_{2}(30 \overline{1}),(\mathrm{b}) \mathrm{h}-\mathrm{PbTiO}(30 \overline{1}),(\mathrm{c}) \mathrm{t}-\mathrm{O}_{2}(30 \overline{1})$, and (d) t-PbTiO $(30 \overline{1})$. The colored vectors indicate $\mathbf{P}^{i j}$ with the rotation angle $\theta^{i j}$ color-matched according to the scale bar.

To explain the formation of the sandwich-like distributions along the $\left[\begin{array}{lll}1 & 0 & 0\end{array}\right]$ direction, the contributions from $P_{z}$ and $P_{x}$ are separately plotted for the h- $\mathrm{O}_{2}(30 \overline{1})$ step as an example (Fig. 8). The contributions highlight the role of the Néel-like polarizations to the bound charge. The h-O $\mathrm{O}_{2}(30 \overline{1})$ step without the Néel-like polarization distribution has a high positive bound charge density ( $\rho_{\max }=7.4 \times 10^{8} \mathrm{C} / \mathrm{m}^{3}$ ), which would induce a local depolarization field creating a tail-to-tail $P_{x}$ distribution and hence a Néel-like polarization distribution. In contrast, a Néel-like polarization distribution induces negative bound charges $\left(\rho_{\min }=-4.5 \times 10^{8} \mathrm{C} / \mathrm{m}^{3}\right)$, which would in turn greatly reduce the positive bound charges at the step. Because the negative bound charges are more dispersive than the positive ones in the normal direction, the distribution of the bound charges in total is sand-wich-like.

## D. Energies of steps and barriers for their motion

In this section, we discuss the energy of the steps based on the calculated energies. In an approximation, we treated the $180^{\circ} \mathrm{DW}$ with a step in a $12 \times 1 \times 10$ supercell as a combination of a ( $\left.30 \begin{array}{l}1 \\ 1\end{array}\right) \mathrm{DW}$ and an ideal PbO -centered $\left(\begin{array}{lll}1 & 0 & 0\end{array}\right)$


FIG. 7. Bound charge density distributions for step models (a) h- $\mathrm{O}_{2}(30 \overline{1})$, (b) h-PbTiO (3 $0 \overline{1})$, (c) $t-\mathrm{O}_{2}(30 \overline{1})$, and (d) $t-\mathrm{PbTiO}(30 \overline{1})$. The density unit is $10^{8} \mathrm{C} / \mathrm{m}^{3}$.

DW, the areas of which are about $S_{1}=a_{0} \sqrt{a_{0}^{2}+\left(3 c_{0}\right)^{2}}$ and $S_{2}=7 a_{0} c_{0}$, respectively. Therefore, the averaged energy of a pair of (30 $\overline{1}$ ) DWs can be calculated from

$$
\begin{equation*}
\bar{E}_{\mathrm{dw} 1}=\frac{E_{\mathrm{tot} 1}-E_{\mathrm{bulk}}-2 S_{2} E_{\mathrm{dw} 2}}{2 S_{1}} \tag{5}
\end{equation*}
$$

where $E_{\text {tot1 }}$ denotes the energy of a $12 \times 1 \times 10$ supercell with two steps on the DWs, $E_{\text {bulk }}$ denotes the energy of an equivalent supercell without steps or DWs, and $E_{\text {dw } 2}$ denotes the energy of formation of the ideal PbO -centered $\left(\begin{array}{lll}1 & 0 & 0\end{array}\right)$ DW. The latter is calculated using

$$
\begin{equation*}
E_{\mathrm{dw} 2}=\frac{E_{\mathrm{tot} 2}-E_{\mathrm{bulk}}}{2 S}, \tag{6}
\end{equation*}
$$

where $E_{\text {tot } 2}$ denotes the energy of a $12 \times 1 \times 10$ supercell with two ideal PbO -centered ( $\left.\begin{array}{lll}1 & 0 & 0\end{array}\right) \mathrm{DWs}$ and $S=10 a_{0} c_{0}$ is the area of the $\left(\begin{array}{ll}1 & 0\end{array}\right)$ DW. Table III lists the calculated energies of different DWs. Note that the averaged energy of the steps

TABLE II. Angle $\alpha$ and corresponding extremum of the bound charge density at step centers.

| Step | $\mathrm{h}-\mathrm{O}_{2}\left(\begin{array}{llll}3 & 0 & \overline{1}\end{array}\right)$ | $\mathrm{h}-\mathrm{PbTiO}(30 \overline{1})$ | $\mathrm{t}-\mathrm{O}_{2}\left(\begin{array}{lll}0 & \overline{1}\end{array}\right)$ | $\mathrm{t}-\mathrm{PbTiO}(30 \overline{1})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\alpha$ (degree) | 21.7 | 21.0 | 19.9 | 18.5 |
| $\rho\left(10^{8} \mathrm{C} / \mathrm{m}^{3}\right)$ | 2.8 | 2.2 | -2.8 | -2.6 |



FIG. 8. Bound charge density maps of the h- $\mathrm{O}_{2}$ ( $30 \overline{1}$ ) step decomposed with respect to contributions from (a) $P_{z}$ and (b) $P_{x}$. The density unit is $10^{8} \mathrm{C} / \mathrm{m}^{3}$.
is obviously larger than the energies of both the $180^{\circ}$ and $90^{\circ}$ DWs. The energy difference $E_{\text {step }}=\bar{E}_{\mathrm{dw} 1}-E_{\mathrm{dw} 2}=20 \mathrm{~mJ} / \mathrm{m}^{2}$ can be considered as the energy for the formation of a pair of steps on the parent $180^{\circ}(100) \mathrm{DW}$.

The step motion might be considered as the alternating appearance of the two step models, $\mathrm{O}_{2}\left(\begin{array}{lll}3 & 0 & \overline{1}\end{array}\right)$ and PbTiO ( $30 \overline{1}$ ). The barriers for the step motion can then be calculated from the energy difference between the two step models, similar to the calculation of barriers for the motion of an ideal DW. ${ }^{16}$ The barrier for the motion of the tail-to-tail step can also be expressed as the energy difference between the t $\mathrm{O}_{2}(30 \overline{1})$ and $\mathrm{t}-\mathrm{PbTiO}(30 \overline{1})$ models, yielding

$$
\begin{equation*}
\Delta E_{\mathrm{h}}=\frac{\left|E_{\mathrm{tot}}(\mathrm{~h}-\mathrm{PbTiO})-E_{\mathrm{tot}}\left(\mathrm{~h}-\mathrm{O}_{2}\right)\right|}{S_{\mathrm{dw}}} \tag{7}
\end{equation*}
$$

and

$$
\begin{equation*}
\Delta E_{\mathrm{h}}=\frac{\left|E_{\mathrm{tot}}(\mathrm{t}-\mathrm{PbTiO})-E_{\mathrm{tot}}\left(\mathrm{t}-\mathrm{O}_{2}\right)\right|}{S_{\mathrm{dw}}} \tag{8}
\end{equation*}
$$

where $E_{\text {tot }}$ denotes the total energy of the corresponding supercells and $S_{\mathrm{dw}}$ indicates the area of the DW moved, which is equal to $a_{0} c_{0}$ according to the following analysis.

Because the continual motion of the steps on the DWs produces the motion of the DW, ${ }^{7-9}$ the motion of a step can be equivalently regarded as the motion of a DW segment. The step motion from one $\mathrm{h}-\mathrm{O}_{2}(30 \overline{1})$ plane to an adjacent plane [green arrow in Fig. 9(a)] is equivalent to the motion of a DW segment with a vertical length of $c_{0}$ from one PbO (100) plane to an adjacent plane (black arrow), which enables the energy barriers of the step motion and the DW motion to be compared [Fig. 9(b)]. The switched volumes are exactly the same; both are $a_{0}{ }^{2} c_{0}$. The barrier for the DW

TABLE III. Calculated energies of different DWs with results from previous work.

| Structure | $180^{\circ}(301) \mathrm{DW}$ | $180^{\circ}(100) \mathrm{DW}$ | $180^{\circ}(100) \mathrm{DW}^{18}$ | $90^{\circ} \mathrm{DW}^{16}$ |
| :--- | :---: | :---: | :---: | :---: |
| $E\left(\mathrm{~mJ} / \mathrm{m}^{2}\right)$ | 145 | 125 | 128 | 35 |



FIG. 9. Schematics of the motion of (a) the head-to-head step and (b) the ideal $180^{\circ} \mathrm{DW}$. The dash and solid lines mark the initial and final positions and the dotted arrows indicate the direction of movement of the DWs (black) and steps (green), respectively. The white-on-blue arrows denote the direction of $P_{z}$.
motion for the (100)-oriented $180^{\circ}$ DWs in PTO can be calculated from

$$
\begin{equation*}
\Delta E_{\mathrm{dw}}=\frac{\left|E_{\mathrm{tot}}(\mathrm{PbO})-E_{\mathrm{tot}}\left(\mathrm{TiO}_{2}\right)\right|}{2 S_{\mathrm{dw}}} \tag{9}
\end{equation*}
$$

The appearance of the factor 2 in the denominator reflects the fact that we actually consider instances of the simultaneous motion of two DWs in a supercell ${ }^{16}$ by comparing the total energies of the two models. In each step model, one step is fixed and the other is moved, thus only $S_{\mathrm{dw}}$ appears in Eqs. (7) and (8). As a consequence, barriers $\Delta E_{\mathrm{h}}=3 \mathrm{~mJ} / \mathrm{m}^{2}$ and $\Delta E_{\mathrm{t}}=2 \mathrm{~mJ} / \mathrm{m}^{2}$ were obtained. Both $\Delta E_{\mathrm{h}}$ and $\Delta E_{\mathrm{t}}$ are much smaller than the barrier $\Delta E_{\mathrm{dw}}=37 \mathrm{~mJ} / \mathrm{m}^{2}$ for the motion of the ideal (100) $180^{\circ} \mathrm{DW},{ }^{15}$ in good agreement with the previous theory that the motion of the $180^{\circ}$ DWs proceeds with the continual motion of steps on the DWs than moving the entire $180^{\circ} \mathrm{DW}$. Compared with the energy for the formation of a pair of steps on the parent $180^{\circ}\left(\begin{array}{ll}1 & 0\end{array}\right)$ DW (about $20 \mathrm{~mJ} / \mathrm{m}^{2}$ ), the barriers for the step motion are much lower. That is, the formation of the charged ( $\left.\begin{array}{ll}3 & 0 \\ 1\end{array}\right)$ step on the $(100) \mathrm{DW}$ is the controlling process of the DW motion. Once an electric field is strong enough to form a charged $\left(\begin{array}{ll}3 & 0 \\ 1\end{array}\right)$ step on the $\left(\begin{array}{ll}1 & 0\end{array} 0\right) \mathrm{DW}$, the step is able to move easily.

## IV. CONCLUSIONS

Using first-principles calculations, we systematically studied the structures and polarization distributions of the head-to-head and tail-to-tail charged steps on the (100)-oriented $180^{\circ}$ DWs in PTO and calculated the barriers for the motion of the steps. Our main conclusions are
(1) The head-to-head and tail-to-tail steps both slope and have approximate Miller indices ( $30 \overline{1}$ ).
(2) The polarization distribution around the charged steps is Ising-Néel-like. The significant Néel-like rotation of the polarization is induced by the bound charges at the steps; the polarization rotation in turn greatly reduces the bound charge.
(3) The calculated barriers for the step motions along the DWs are much smaller than those for the motion of the $180^{\circ}$ DWs as a whole, which implies the step motions on the DW are the dominant factor in the motion of DWs.

## ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (Nos. 51671194, 51571197, 51371176, and 51401212) and the Frontier Science Key Programs of the Chinese Academy of Sciences (QYZDJ-SSW-JSC010). The authors are grateful to Dr. T. Sasaki of the National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Japan for his revision. D. Chen acknowledges the Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase) under Grant No. U1501501. We thank Richard Haase, Ph.D, from Liwen Bianji, Edanz Group China (www.liwenbianji.cn/ac), for editing the English text of a draft of this manuscript.
${ }^{1}$ J. F. Scott and C. A. Paz de Araujo, Science 246, 1400 (1989); J. F. Scott, Ferroelectric Memories (Springer, Heidelberg, Germany, 2000).
${ }^{2}$ M. E. Lines and A. M. Glass, Principles and Applications of Ferroelectrics and Related Materials (Oxford University Press, Oxford, 2001).
${ }^{3}$ W. J. Merz, Phys. Rev. 95, 690 (1954).
${ }^{4}$ M. Dawber, K. M. Rabe, and J. F. Scott, Rev. Mod. Phys. 77, 1083 (2005).
${ }^{5}$ C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Science 303, 488 (2004).
${ }^{6}$ P. Gao, J. Britson, J. R. Jokisaari, C. T. Nelson, S.-H. Baek, Y. Wang, C.B. Eom, L.-Q. Chen, and X. Pan, Nat. Commun. 4, 2791 (2013).
${ }^{7}$ R. C. Miller and G. Weinreich, Phys. Rev. 117, 1460 (1960).
${ }^{8}$ Y.-H. Shin, I. Grinberg, I.-W. Chen, and A. M. Rappe, Nature (London) 449, 881 (2007).
${ }^{9}$ S. Liu, I. Grinberg, and A. M. Rappe, Nature (London) 534, 360 (2016).
${ }^{10}$ T. Tybell, P. Paruch, T. Giamarchi, and J.-M. Triscone, Phys. Rev. Lett. 89, 097601 (2002).
${ }^{11}$ C.-L. Jia, S.-B. Mi, K. Urban, I. Vrejoiu, M. Alexe, and D. Hesse, Nat. Mater. 7, 57 (2008).
${ }^{12}$ G. De Luca, M. D. Rossell, J. Schaab, N. Viart, M. Fiebig, and M. Trassin, Adv. Mater. 29, 1605145 (2017).
${ }^{13}$ A. Angoshtari and A. Yavari, J. Appl. Phys. 108, 084112 (2010).
${ }^{14}$ Y. Yu, X. Zhang, Y. G. Zhao, N. Jiang, R. Yu, J. W. Wang, C. Fan, X. F. Sun, and J. Zhu, Appl. Phys. Lett. 103, 032901 (2013).
${ }^{15}$ S. Pöykkö and D. J. Chadi, Appl. Phys. Lett. 75, 2830 (1999).
${ }^{16}$ B. Meyer and D. Vanderbilt, Phys. Rev. B 65, 104111 (2002).
${ }^{17}$ A. Lubk, S. Gemming, and N. A. Spaldin, Phys. Rev. B 80, 104110 (2009).
${ }^{18}$ R. K. Behera, C.-W. Lee, D. Lee, A. N. Morozovska, S. B. Sinnott, A. Asthagiri, V. Gopalan, and S. R. Phillpot, J. Phys.: Condens. Matter 23, 175902 (2011).
${ }^{19}$ D. Lee, R. K. Behera, P. Wu, H. Xu, Y. L. Li, S. B. Sinnott, S. R. Phillpot, L. Q. Chen, and V. Gopalan, Phys. Rev. B 80, 060102 (2009).
${ }^{20}$ Y. J. Wang, D. Chen, Y. L. Tang, Y. L. Zhu, and X. L. Ma, J. Appl. Phys. 116, 224105 (2014).
${ }^{21}$ J. C. Wojdeł and J. İniguez, Phys. Rev. Lett. 112, 247603 (2014).
${ }^{22}$ T. Xu, T. Shimada, Y. Araki, J. Wang, and T. Kitamura, Nano Lett. 16, 454 (2016).
${ }^{23}$ W. Kohn and L. Sham, Phys. Rev. 140, A1133 (1965).
${ }^{24}$ D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
${ }^{25}$ P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
${ }^{26}$ G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
${ }^{27}$ G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
${ }^{28}$ G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
${ }^{29}$ H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
${ }^{30}$ W. Cao, G. R. Barsch, and J. A. Krumhansl, Phys. Rev. B 42, 6396 (1990).
${ }^{31}$ W. Cao and L. E. Cross, Phys. Rev. B 44, 5 (1991).
${ }^{32}$ M. Li, Y. Gu, Y. Wang, L.-Q. Chen, and W. Duan, Phys. Rev. B 90, 054106 (2014).
${ }^{33}$ E. A. Eliseev, A. N. Morozovska, G. S. Svechnikov, V. Gopalan, and V. Y. Shur, Phys. Rev. B 83, 235313 (2011).
${ }^{34}$ E. A. Eliseev, A. N. Morozovska, G. S. Svechnikov, P. Maksymovych, and S. V. Kalinin, Phys. Rev. B 85, 045312 (2012).
${ }^{35}$ Y. J. Wang finished the calculations on the extremum of bound charge density at Néel-like polarizations around (100) $180^{\circ}$ DWs.


[^0]:    ${ }^{\text {a) }}$ Authors to whom correspondence should be addressed: dchen@imr.ac.cn and xlma@imr.ac.cn

