Atomistic modeling of flexoelectricity in periclase

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(Received 25 May 2014, revised manuscript received 10 December 2015, published 8 January 2016)

Flexoelectricity is evolution of a macroscopic polarization due to a strain *gradient*. We present a molecular dynamics study of flexoelectricity in the cubic ionic MgO periclase phase. Using an effective interaction force field with polarizable oxygen atoms and applying it to an inhomogeneously strained periclase sample, we detect a collective flexoelectric response of the oxygen dipole moments in visualizations. This induced polarization depends linearly on the strength of the strain gradient as well as the primary polarization, which is caused by the displacement of the ion charges. By three different inhomogeneous deformation modes all three flexoelectric coefficients of periclase are determined.

DOI: 10.1103/PhysRevB.93.024105

Metal oxides, e.g., alumina or silica, are ubiquitous in industrial applications and thus in our daily life. Therefore, metal oxides are much studied, in particular also by atomistic numerical simulations. One challenge thereby are the long range electrostatic forces due to ionic charges and the deformable electron shell of the oxygen atoms.

In an attempt to develop realistic effective potentials for metal oxides, Beck et al. [1] applied a method of Tangney and Scandolo [2] (TS), where the oxygen ions not only are endowed with a valence charge but also with a polarizability. The method was used and applied by Hocker et al. [3] to develop potentials for and to study crack propagation in α alumina (Al₂O₃). The simulation results were visualized by Grottel et al. [4] with the software package MegaMol [5]. In the visualization, the aluminum ions were presented by spheres and the oxygen ions by arrows, indicating the direction of the induced dipole moment. Surprisingly, regions in front of the crack tip showed ferroelectric and antiferroelectric domains, although α -alumina is not piezoelectric. We have inspected the phenomenon closer and have come to the conclusion that the simulations show a flexoelectric effect, i.e., induction of an electric polarization not by strain, but by a strain gradient. In the following we observed the effect in a more controlled way in the simple cubic oxide periclase, crystalline magnesia (MgO) with sodium chloride structure, where we applied three well defined displacement modes. We could measure all three flexoelectric coefficients. This is a striking example, where visualization leads to the discovery of new phenomena.

I. PIEZOELECTRICITY

In 1880 Pierre and Jacques Curie discovered that a voltage emerges from the deformation of a material [6,7]. In a microscopic view, oriented electrostatic dipole moments build up in dielectric materials due to external strain. In general, the linear piezoelectric coupling between polarization P and strain ε can be expressed by a three-stage tensor d, $P_i = d_{ijk}\varepsilon_{jk}$. The corresponding free energy density (with the electric field **E**) can be written as [8]

$$f_{\text{piezo}} = -\boldsymbol{E} \cdot \boldsymbol{P} = -E_i d_{ijk} \varepsilon_{jk}.$$
 (1)

As upon inverting spatial coordinates the electric field E changes sign, but not the strain tensor ε , the free energy

[Eq. (1)] is not inversion invariant, and piezoelectricity is forbidden in crystalline systems with inversion symmetry.

II. FLEXOELECTRICITY

However, even in inversion-symmetric systems and thus in principle in all crystalline dielectrics a polarization can develop due to response to a strain gradient $\varepsilon_{ik,l}$ [9], or, as used in many publications and also here, as response to the second derivative of the displacement field $u_{i,kl}$ [10,11] (for the relation between the two conventions see [12,13]). The effect is denoted *flexoelectricity*. First predicted by Mashkevich and Tolpygo [14] and phenomenologically described by Kogan [15], flexoelectricity establishes a new material class for industrial products that are based on generating voltage by deformation. In the bulk the flexoelectric effect is small, but it becomes important in nanocrystals or epitaxial thin films where the strain gradient can take large values [16]. With suitable geometries the flexoelectric effect can be used to produce piezoelectric metamaterials even with centrosymmetric compounds [17]. Recently, in a nanoscale volume of a ferroelectric film, polarization could be switched mechanically due to the stress gradient generated by the tip of an atomic force microscope [18]. Other phenomena, where flexoelectricity influences properties, are the modification of the dielectric constant in nanodevices [19,20] and generally piezoelectriclike responses in devices made out of nonpiezoelectric materials [21,22]. For a recent review see Zubko et al. [23].

In linear response flexoelectricity is described by a fourth-rank tensor μ ,

$$P_i = \mu_{iikl} u_{i,kl}.$$
 (2)

In a crystal of cubic symmetry, the coupling tensor

$$\mu_{ijkl} = (\mu_{11} - \mu_{12} - 2\mu_{44})\delta_{ijkl} + \mu_{12}\delta_{ij}\delta_{kl} + \mu_{44}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})$$
(3)

 $(\delta_{ijkl} \text{ is 1 for all indices equal and zero otherwise})$ has only three independent components [11,12]. There is no piezoelectric coupling.

The flexoelectric coefficients are difficult to measure. In experiments [10,24–28], as a rule only one or two have been determined. Numerical simulations are a useful supporting

tool. Although the analytical description [29–32] and *ab initio* [13,33–36] studies have advanced, no molecular dynamics (MD) simulations have been performed yet. There exists one single atomistic approach [37], where an *ab initio* based polarizable force field for barium titanate was adopted to model dipole orientation phenomena, with a focus on the dependence of polarization on the sample size.

In ionic solids one has to discern two kinds of polarization: the *primary* one, which results from the asymmetric displacement of the ionic charges due to the strain gradient, and an *induced* one due to the deformation of the electronic orbits. Oxygens are particularly appealing, because the O atom is strongly polarizable. We are interested in the relation between the two contributions. In the literature different notations are used. In the first-principle studies of flexoelectricity by Hong and Vanderbilt (HV) [13] the *lattice* or *relaxed-ion* part, which results from internal sublattice shifts, is to be identified with our primary polarization. Their pure *electronic* or *frozen ion* part, which depends on octupole moments of the charge density [34], corresponds to our induced polarization as well as the *shell contribution* of Askar *et al.* [38].

III. SIMULATIONS

Here we present MD simulations of the oxygen periclase, performed with the MD code ITAP Molecular Dynamics [39]. For the ions of magnesia, a highly accurate, effective interaction force field has been developed recently [1]. The TS model, upon which it is based, appreciably increases accuracy for collective phenomena in metal oxide systems [40,41]. In this TS approach, the dipole moments of the oxygen ions depend on the local electric field of the surrounding valence charges and dipoles. They are calculated by a self-consistent iterative algorithm. A dipole moment p_i^n at position r_i in iteration step *n* consists of a long range induced part due to an electric field $E(r_i)$ and a short range induced part p_i^{SR} due to the short range interactions between charges q_i and q_j . Following Rowley *et al.* [42], this contribution is given by

$$\boldsymbol{p}_i^{\text{SR}} = \alpha_i \sum_{j \neq i} \frac{q_j \boldsymbol{r}_{ij}}{r_{ij}^3} f_{ij}(r_{ij}) \tag{4}$$

with

$$f_{ij}(r_{ij}) = c_{ij} \sum_{k=0}^{4} \frac{(b_{ij}r_{ij})^k}{k!} e^{-b_{ij}r_{ij}}.$$
 (5)

 α_i is the polarizability of atom *i*; $f_{ij}(r_{ij})$ was introduced *ad hoc* to account for multipole effects of nearest neighbors and is a function of very short range. α_i, b_{ij}, c_{ij} and the valence charges q_j are parameters of the force field [1]. Together with the long ranged induced part, one obtains

$$\boldsymbol{p}_{i}^{n} = \alpha_{i} \boldsymbol{E} \left(\mathbf{r}_{i}; \left\{ \boldsymbol{p}_{j}^{n-1} \right\}_{j=1,N}, \left\{ \boldsymbol{r}_{j} \right\}_{j=1,N} \right) + \boldsymbol{p}_{i}^{\text{SR}}.$$
 (6)

 $E(r_i)$ is the electric field at position r_i , which is determined by the valence charges and the dipole moments p_j^{n-1} of the previous iteration step. The long-range electrostatic forces between charges and dipoles [43] were treated with the Wolf summation [44]. The Wolf method is a meanwhile well established O(N)-scaling approach for fast and accurate simulations of ionic bulk systems.

IV. RESULTS

The three flexoelectric constants μ_{11} , μ_{12} , and μ_{44} of periclase can be determined by applying three different inhomogeneous deformation modes to the ionic system [10]. The corresponding displacements are

(a)
$$u_z = k \frac{x^2}{2}; \quad P_z = P_3 = k \mu_{12},$$
 (7)

(b)
$$u_z = k \frac{z^2}{2}; \quad P_z = P_3 = k \mu_{11},$$
 (8)

(c)
$$u_x = kxz; \quad P_z = P_3 = 2k\mu_{44},$$
 (9)

with the polarization calculated by Eq. (2). The constant k rules the strength of the displacement and its gradient. The corresponding geometries are illustrated in Fig. 1. For the MD simulations a periclase sample of about 120 000 atoms is created (Fig. 1). It is deformed by shifting all atoms by the above quadratic functions from their unperturbed positions.

The primary polarization is calculated as the sum

$$\boldsymbol{P}^{p} = \frac{1}{V} \sum_{i=1}^{N} q_{i} \boldsymbol{r}_{i} = \frac{1}{V} \sum_{i=1}^{N} q_{i} (\boldsymbol{r}_{0i} + \boldsymbol{u}_{i}) = \frac{1}{V} \sum_{i=1}^{N} \boldsymbol{u}_{i} q_{i},$$
(10)

with q_i denoting the ion charges and their positions r_i after the deformation and V cubic volumes of different sizes inside the samples, avoiding surface charges. r_{0i} are the atomic positions of the undeformed sample. The displacements u_i are functions of the unperturbed atomic coordinates according to Eqs. (7)–(9). The first sum vanishes, since if no shift is executed the charges are arranged inversion symmetric. In case of mode (a) u_i contains the square of the undeformed x positions, which is always positive. Since the charge values q_i alternate in sign, the last sum (running over the undeformed lattice) is zero, too. For the modes (b) and (c) the same result holds: With the deformation fields from Eq. (7) to (9) the local inversion symmetry is not broken and thus no primary polarization occurs. In contrast, an induced polarization is allowed and is observed (Fig. 2).

Hence, for a primary polarization to exist, additional internal sublattice shifts within the unit cell are required, which follow after relaxation, while the initial uniform strain



FIG. 1. The undeformed samples (dashed lines) are blocks of $210.5 \times 42.1 \times 126.3$ Å containing 120 000 atoms. They are deformed by the displacement modes given by Eqs. (7)–(9) (red lines). The coordinate system points along the cubic fourfold axes of the system. When applied to a periclase sample, they allow us to determine the three superscribed flexoelectric constants. Samples (a) and (c) are continued periodically along the *y*, sample (b) along *x* and *y* directions. The open surfaces are neutral.



FIG. 2. The induced dipoles of the oxygen atoms are oriented in case of displacement (a) along the negative z direction, while for displacement (b) they point along the positive z axis. This is in accord with the direction of electric field, as illustrated in Fig. 5. The color coding done by MegaMol visualizes the orientation of the arrows.

is preserved [11,13]. There is no unique approach in the literature of how to maintain the applied strain gradient and simultaneously to execute the relaxation for obtaining the desired sublattice shifts. HV [13] introduced for the lattice or relaxed-ion polarization, which corresponds to the primary one, artificial forces acting on the atoms of the unit cell after the induced displacements occurred. Such "force patterns" can be chosen differently. A mass-weighted choice seems to be most reasonable one. But the flexoelectric constants depend sensibly on the chosen force pattern as discussed by HV.

We solved the puzzle by adjusting the simulations to the experimental setup. Where possible, the inhomogeneous displacements were only applied to the atoms of the first surface layers. Then the bulk atoms were relaxed.

Thus for the modes (a) and (c) three steps were executed to gain a nonvanishing primary polarization: (1) All atoms of the sample are displaced by the quadratic functions of their former lattice position given by Eqs. (7) and (9). (2) The inhomogeneous strain is kept by locking the surface atoms. For mode (b) such a surface stabilization is not possible. (3) A relaxation with fixed surface layers is performed. PHYSICAL REVIEW B 93, 024105 (2016)



FIG. 3. The primary polarization converges after 60 000 MD steps by using the microconvergence integrator (mik) in IMD. However, the induced polarization reaches its fixed value from the beginning. The illustration is done here for mode (a) and for $k = 1.35 \times 10^6$ /m.

For the relaxation a microconvergence integrator (mik) is used. If an atom passes the minimum in the potential landscape, its velocity is reset to zero [39]. Close to 0 K a finite homogeneous polarization arises. After 60 000 MD steps the primary polarization converges to a fixed value (see Fig. 3). The same procedure was executed for different k values of the displacement fields. As expected, a linear dependence of polarization and strain from Eq. (2) follows, which is shown in Fig. 4(a). From the slope of the lines the primary part of the flexoelectric constants can be extracted.

The induced polarization, denoted as P^{TS} , is calculated by Eqs. (6) and (4). As the primary polarization, it points along the three axis after applying the nonlinear deformation modes (a), (b), and (c). Since the short range induced dipole moments p_i^{sr} of Eq. (4) turn out to be one magnitude less than the long-range ones, the sign of the total induced moments essentially depends on the direction of the electric field at the oxygen positions. This direction is made plausible by the displacement of already nearest neighbor Mg²⁺ charges in Fig. 5. In case (a) it is negative, in case (b) positive [45].

The three steps for determining the primary polarization are not applicable to deformation mode (b), because the lattice planes will relax to equidistant separations. The induced polarization depicted in Fig. 2 resulted after a few MD steps from an initial configuration (b) and before the ion positions had changed appreciably.

To obtain the missing constant μ_{11} we apply the bending mode (a) and its boundary conditions to a sample rotated by $\pi/4$. The measured flexoelectric constant is a linear combination of μ_{12} , μ_{11} , and μ_{44} .

As a first step the sample is regarded in the rotated coordinate system. The corresponding rotation matrix takes the form

$$\underline{\mathbf{R}} = \begin{pmatrix} 1/\sqrt{2} & 0 & 1/\sqrt{2} \\ 0 & 1 & 0 \\ -1/\sqrt{2} & 0 & 1/\sqrt{2} \end{pmatrix}.$$
 (11)



FIG. 4. In (a) the primary polarization P_3^p is plotted against the strength k of the applied strain gradient, while in (b) the induced polarization P_3^{TS} obtained by the TS model is illustrated. Each point follows after a relaxation of 60 000 MD steps using the microconvergence integrator (mik) in IMD. As expected, in all deformation modes (a), (c), and (a') the polarization is a linear function of the strength of the strain gradient. For μ_{11} the $\pi/4$ -rotated sample was also deformed by mode (a). From the slope of the lines the flexoelectric constants μ_{12} , μ_{44} , and $\mu'_{3'3'1'1'}$ are derived.

The crystal surface still remains neutral as in the former, unrotated case. In a second step the deformation mode (a') is executed:

$$u'_{z'} = k \frac{{x'}^2}{2},\tag{12}$$

where the prime indicates the new coordinate system. In analogy to Eq. (7) the resulting polarization points along the z' direction:

$$P'_{3'} = \mu'_{3'3'1'1'}k, \tag{13}$$

with $\mu'_{3'3'1'1'}$ being the flexoelectric constant in the rotated system. By use of Eq. (11) $\mu'_{3'3'1'1'}$ is expressed as a function



FIG. 5. The direction of the dipoles in the TS model is essentially given by the electric field E as the long-range induced polarization [see Eqs. (4) and (6)] dominates the short-range one. Why the dipoles in Fig. 2 are oriented oppositely can be understood by considering the electric field of two Mg²⁺ atoms (red) at the position of the polarizable O²⁻ atom (blue) in between. On the left side the bending case (a) of Fig. 1 is shown in one plane. The E field points downwards. However, for the stretching displacement (b) from Eq. (7) (right) it points upwards.

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of the nonprimed components:

(a)

$$\mu'_{3'3'1'1'} = \mu_{ijkl} R_{i3'} R_{j3'} R_{k1'} R_{l1'} = \frac{1}{2} \{\mu_{11} + \mu_{12} - 2\mu_{44}\}.$$
(14)

In summary, as Fig. 4 shows, the magnitude $P = |\mathbf{P}|$ of the polarization (boundary atoms omitted) scales linearly with the strain gradient. Such a linear dependence has been observed in experiments by Cross [25] for different ionic bulk materials and Baskaran and He for polyvinylidene fluoride films [28]. All flexoelectric constants of periclase can now be determined from the slopes:

$$\mu_{12} = -(2.2 + 9.0)\frac{\text{pC}}{\text{m}} = -11.2\frac{\text{pC}}{\text{m}},$$
(15)

$$\mu_{11} = -(2.4 - 11.0)\frac{\text{pC}}{\text{m}} = 8.6\frac{\text{pC}}{\text{m}},\tag{16}$$

$$\mu_{44} = -(10.1 + 6.6)\frac{\text{pC}}{\text{m}} = -16.7 \frac{\text{pC}}{\text{m}},$$
 (17)

where the first entry in the bracket results from the primary and the second from the induced polarization. μ_{11} was derived from $\mu'_{3/3/1/1/1}$ via μ_{12} and μ_{44} by Eq. (14).

The sign of μ_{11} differs from the other flexoelectric constants because of the dominant positive induced part μ_{11}^{TS} . Why this part is positive is explained by Fig. 5.

The long-range and the short-range part of the induced dipole moments in the TS model [Eqs. (4) and (6)] have correspondences in the shell model as employed, e.g., by Askar *et al.* [38]. Both methods mimic a polarization caused by a macroscopic electric field and one by approaching ion cores. In the shell model calculations the polarization due to sublattice shifts and hence the primary polarization is not considered [11].

For the chlorides NaCl and KCl, isostructural to MgO, flexoelectric constants have been calculated also with the shell

(b)

model [11]. They are of the same sign and order of magnitude as the ones here for induced polarization. The constants for the piezoelectric cubic semiconductors GaAs, GaP, and ZnS are larger by about a factor 5 [11]. All these systems are weak flexoelectrics compared with the high dielectric perovskites BaTiO₃ and SrTiO₃ in their cubic phase, where *ab initio* calculations [11] and experiments [24,26] report values between 150 and 10⁷ pC/m.

V. CONCLUSION

We have demonstrated flexoelectric response of an inhomogeneously strained periclase sample by molecular dynamics. PHYSICAL REVIEW B 93, 024105 (2016)

Both the direction of the collective dipole orientation and the linearity of the material's response are in agreement with theory. With our model we were able to determine the flexoelectric coupling coefficients μ_{12} , μ_{11} , and μ_{44} .

ACKNOWLEDGMENTS

The authors thank Katrin Scharnowski, Sebastian Grottel, and Michael Krone for the collaboration regarding the visualization with MegaMol. Thanks also to Alexander Kiselev for illuminating discussions. Support from the DFG through Collaborative Research Centre 716, Project B.1 is gratefully acknowledged.

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