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Abstract
We present *ab initio* calculations of the longitudinal flexoelectricity for $BaTiO_3$ and $SrTiO_3$ using a direct approach. The calculated value for $SrTiO_3$ agrees with recently reported measurements. For $BaTiO_3$, however, the theoretical values are smaller than the measured ones; possible reasons for the discrepancy are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Inhomogeneous strains can induce dielectric polarization in all insulators thanks to the so-called flexoelectric effect, which couples polarization to strain gradient. Flexoelectricity[6] was theoretically described more than 40 years ago by Kogan [2]. Although it is a universal property of all dielectrics, and not just piezoelectric ones, flexoelectricity is nevertheless a relatively small effect compared with piezoelectricity, and it has generally been overlooked until quite recently; it is only in this decade that the first direct measurements of polarization induced by bending have been reported [3–6], although it is worth mentioning that the reverse effect of a strain gradient (bending) induced by polarization had been measured by Bursian as far back as 1968 [7].

Interest in flexoelectricity is now growing rapidly due to the confluence of two factors: (i) because it scales with dielectric constant [2, 8], it can be large in high permittivity materials such as ferroelectrics and relaxors, and (ii) because it is proportional to strain gradient, flexoelectricity can be huge in the nanoscale, since the same strain relaxed over

a few nanometers yields a much bigger gradient than if it were relaxed over a bulk scale. Flexoelectricity due to either extrinsic causes such as epitaxial strain relaxation [9, 10] or intrinsic such as surface tension [11] or curvature [12] is thus apt to be a large influence on the function of nano-ferroelectric memory elements (thin films, nanowires, nanotubes, nanodots). Flexoelectricity also affects the measurement of piezoelectric properties using scanning probe techniques due to the highly inhomogeneous nature of the field around the scanning tips [13, 14]. The flexoelectric effect has been shown to enhance the piezoelectric properties of nanowires [15], and is being explored with a view to make 'piezoelectric' sensors out of materials that are not themselves piezoelectric [16, 17].

The typical way of measuring flexoelectric coefficients consists in bending beam-shaped ceramics or crystals and measuring the bending-induced polarization [3–6]. However, it has been shown that bending experiments alone cannot determine the full flexoelectric tensor, even for simple cubic symmetries, and that at least one of the three flexoelectric coefficients must be independently measured by a different method [19]. It is therefore imperative to find new ways of measuring flexoelectricity. One potential route to generate

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[6] Throughout this paper we refer only to flexoelectricity as defined for solid crystals, leaving out the better known flexoelectric effect of liquid crystals [1].
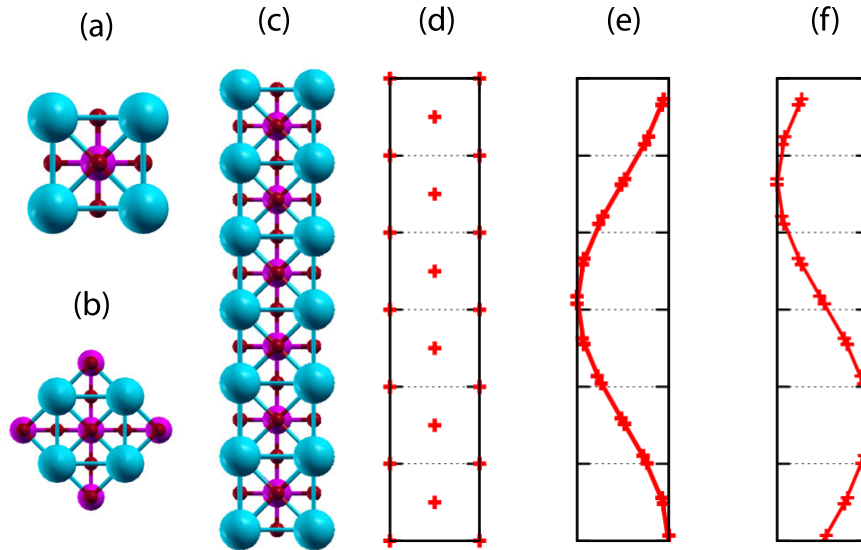
Figure 1. Supercell and strain profile used in the calculations. For BaTiO$_3$, the unit cell contains only one formula unit (a), while for SrTiO$_3$, due to its antiferrodistortive transition at low temperature [18], the in-plane size of the unit cell is doubled (b). (c) and (d) Supercell in xz plan, (e) cosine gradient strain in the supercell, (f) atom displacement in the supercell.

the flexoelectric tensor components may be the use of first-principles calculations. Such an approach would have the double benefit of being able to generate the independent flexoelectric constant needed to characterize the full tensor, and of providing an order-of-magnitude guidance for the values that one should expect from the experiments; thus, if the experimental values are wide off the mark, one can raise 'alarm flags' and search for alternative explanations. This is particularly pertinent in view of the large differences found between the experimental values of flexoelectricity of otherwise similar materials such as BaTiO$_3$ [4] and SrTiO$_3$ [6]. It is also pertinent because, as has been discussed, other effects such as surface piezoelectricity and surface flexoelectricity can mimic and are of the same order of magnitude as bulk flexoelectricity [5, 8].

Theoretical methods for estimating flexoelectricity have been reported very recently by Maranganti and Sharma [20] and Naumov *et al* [21]. The former uses an approach based on relating flexoelectric coefficients to phonons, as originally proposed by Tagantsev [8], while Naumov *et al* use *ab initio* methods to calculate a non-conventional (quadratic) flexoelectric effect in periodically bent boron nitride sheets. Here we use a direct *ab initio* approach that is more direct than the former, and may be regarded as an 'unclamped' generalization of the latter, in order to calculate the longitudinal flexoelectric coefficient, which is the hardest one to measure experimentally [19] and yet the one that determines the performance of the currently made flexoelectric transducers [5, 16].

2. Calculation method

Flexoelectricity is described by a fourth rank tensor that couples the polarization to a strain gradient:

$$P_i = f_{ijkl} \frac{\partial \varepsilon_{kl}}{\partial x_j} \tag{1}$$

where P_i is the flexoelectrically induced polarization, $\partial \varepsilon_{kl}/\partial x_j$ is the strain gradient and f_{ijkl} are the flexoelectric tensor coefficients. In materials with simple cubic symmetries, such as cubic perovskites, there are only three independent tensor coefficients: longitudinal, shear and transverse [3, 6].

The main difficulty in using *ab initio* methods for calculating flexoelectricity is the fact that such calculations require the use of supercells with periodic boundary conditions, whereas a strain gradient, by definition, results in an inhomogeneous distribution of lattice parameters and thus a breaking of the lattice periodicity. In order to circumvent this problem, we construct here an 'accordion' supercell whereby the strain gradient is itself periodic, thus allowing the recovery of the periodic boundary condition. Specifically, the strain profile along the z direction is chosen in the cosine form:

$$\varepsilon(z) = \varepsilon_{\max} \cos \left(2\pi \frac{z}{h} \right) \tag{2}$$

where h is the height of the supercell, $\varepsilon_{\max}$ is the max strain in the supercell. This supercell is depicted in figure 1.

To calculate the flexoelectric effect, we chose the position of $h/4$ of the supercell, where the strain gradient is maximum. Both strain and strain gradient may in principle contribute the local polarization via piezoelectricity and flexoelectricity, respectively[7]. However, the piezoelectric polarization in this unit cell is zero, because the average strain is zero by construction (we also checked the volume of this unit cell after relaxing and confirmed that there was no difference with respect to the unstrained value). Thus, choosing the unit cell at $h/4$ not only provides the maximum flexoelectricity, but also eliminates the piezoelectric contributions.

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[7] BaTiO$_3$ is ferroelectric and, although SrTiO$_3$ is in principle paraelectric (or, strictly speaking, a quantum paraelectric), strain can also induce a phase transition to a ferroelectric state in which piezoelectricity would of course be allowed.
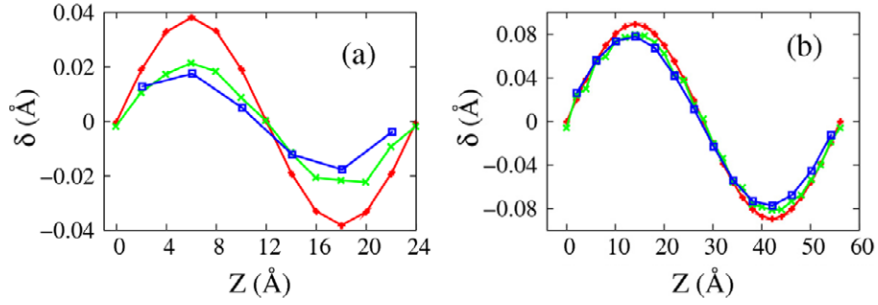
Figure 2. Strain gradient in relaxed BaTiO$_3$ supercells of different vertical size under a strain gradient profile with maximum strain $\varepsilon_{max} = 1\%$; (a) $N = 6$, (b) $N = 14$. The red curves (circles) are the average displacements of the A-site atoms (Ba) with the imposed strain; the green and blue curves (stars and squares, respectively) are the displacements for O and Ti after relaxing the structure to its minimum energy (but keeping the Ba positions fixed). The strain profiles of all the atoms converge as the supercell size increases.

Given a strain profile (equation (2)), the displacement of each atom in the supercell is given by:

$$\delta(z) = \int_0^z \varepsilon(\xi) \, d\xi = \frac{\varepsilon_{max} h}{2\pi} \sin 2\pi \frac{z}{h}. \qquad (3)$$

After applying these displacements the system is relaxed, otherwise only the electronic contribution to flexoelectricity would be probed [21, 22]. Constrains must nevertheless be kept on a subset of atoms to prevent their relaxing back to their equilibrium positions, i.e., to a state with no gradient. In order to impose the strain gradient, we fix the positions of the A-site atoms (Ba or Sr), because they are the ones that participate least in the polarization, while we let all the other atoms relax to their equilibrium positions. The superlattice is then relaxed until the maximum component of the force on any unfixed atom is smaller than 10 meV Å^{-1}. We then use the Born effective charges to calculate the local polarization in each unit cell:

$$P_\alpha = \frac{1}{\Omega} \sum_{\kappa,\beta} Z_{\kappa,\alpha\beta} \delta_{\kappa,\beta} \qquad (4)$$

where P_α is the spontaneous polarization in the α direction, Ω is the unit cell volume, Z_κ is the Born effective charge for atom κ in the bulk material and $\delta_{\kappa,\beta}$ is the displacement of atom κ along the β direction relative to the centrosymmetric structure.

The flexoelectric coefficient is calculated dividing the polarization obtained from equation (4) by the strain gradient obtained from equation (2). While the present construction allows in principle calculating the flexoelectric tensor components f_{1333} and f_{2333}, these are zero by symmetry for both rhombohedral and tetragonal structures [23], so only the longitudinal f_{3333} is analyzed here.

The calculations have been performed within density-functional theory (DFT) and the generalized gradient approximation (GGA) [24] for BaTiO$_3$ and the local density approximation (LDA) [25] for SrTiO$_3$. We used the SIESTA method [26] based on finite-range numerical atomic orbitals, using a double-ζ polarized basis set [27]. Norm-conserving pseudopotentials were used to reproduce the effect of core electrons, including into the valence the semicore: 3s and 3p shells for Ti, 4s and 4p for Sr, 5s and 5p for Ba. The integrals in reciprocal space were well converged with a k-mesh of 12 Ang cutoff, while the integrals in real space used a r-mesh of 350 Ryd cutoff.

3. Results

The performance test for rhombohedral BaTiO$_3$ has been presented in a previous work [28]. In addition, the spontaneous polarization is 0.434×10^{-9} C m^{-1} along [111], very close to previous theoretical results 0.44×10^{-9} C m^{-1} [29] (the experimental result is 0.35×10^{-9} C m^{-1} [30], although this value is very dependent on sample quality and is presently considered less reliable for the purpose of comparison). The obtained lattice parameter for SrTiO$_3$ is $a = 3.865$ Å and $c/a = 1.004$, while the experimental data [31] is $a = 3.898$ Å and $c/a = 1.000\,56$ at 65 K, and the rotational angle of the octahedral around the c axis is 4°, while it is 2.1° experimentally at 4.2 K [32].

After relaxing the constrained structure, the unfixed atom positions are checked to see whether the gradient strain exists still in the relaxed supercell. Figure 2 shows a typical calculation (in this case for BaTiO$_3$ with $\varepsilon_{max} = 1\%$), showing that the A-site displacement profile is indeed transferred into the unconstrained atoms, which means the cosine strain gradient still exists after relaxing. However, figure 2(a) also shows that the gradient of the relaxed atoms is considerably smaller than that of the fixed A-site atoms (Ba or Sr). This has a considerable impact on the calculated value of the flexoelectric coefficient: since this is calculated dividing the polarization over the gradient, a smaller gradient results in a bigger apparent flexoelectric coefficient.

The discrepancy between the gradient values of the fixed and relaxed atoms is largely an artifact caused by the small size of the supercell. Figure 2(b) shows that, for large supercells, the strain gradients of the constrained A-site atoms and the relaxed B-site atoms are almost the same. Indirectly, this also suggests that the choice of atoms to constrain in order to impose the strain gradient, which we decided to be the A-site atoms to be on the safe side as they play little role in the ferroelectric polarization, is in fact largely irrelevant. Figure 3 shows the flexoelectric coefficients for rhombohedral BaTiO$_3$ with different number of unit cells in the supercell. It can be seen that the calculated flexoelectric coefficient is indeed larger when using the relaxed atoms than when using the fixed ones, but also that the difference between the two values decreases with increasing the height of supercell, suggesting that such difference was the artifact of an insufficiently big supercell.
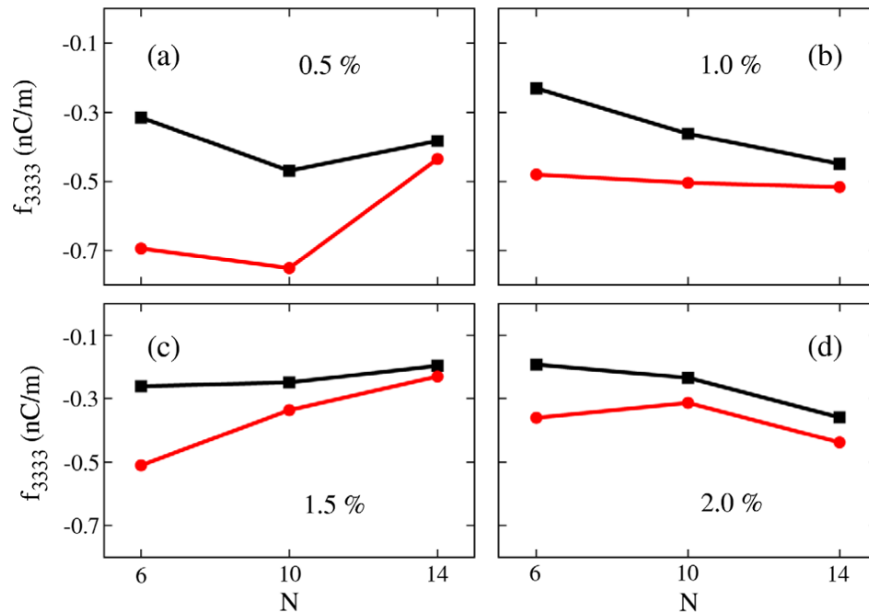
Figure 3. Longitudinal flexoelectric coefficient f_{3333} of rhombohedral BaTiO$_3$ for different supercell sizes ($N = 6$, 10, 14) under various strain gradients ($\varepsilon_{max} = 0.5\%$, 1.0%, 1.5%, 2.0%). In each panel, the black line (up) is for the applied strain, the red line (down) is for the 'relaxed strain' (see text). The two values converge as the supercell size is increased.

The strain gradients of the fixed and relaxed atoms thus converge, and an extrapolation of the flexoelectric coefficients allows estimating $f_{3333} \sim -0.37 \pm 0.03$ nC m^{-1} for BaTiO$_3$ and $f_{3333} \sim -1.38 \pm 0.65$ nC m^{-1} for SrTiO$_3$.

4. Discussion

The flexoelectric coefficients calculated here are all in the order of nC m^{-1}, which is consistent with the theoretical estimation for a simple dielectric [2] and also with recent measurements in SrTiO$_3$ single crystals and ceramics [6, 33]. These values are also on the same order of magnitude as the effective Hamiltonian calculations of Maranganti and Sharma [20]. At first sight, then, the direct *ab initio* approach appears capable of providing reliable estimates of flexoelectric coefficients of SrTiO$_3$, but of course the agreement may be fortuitous, particularly since our calculations are for SrTiO$_3$ at 0 K, whereas the experimental measurements and effective Hamiltonian calculations are for SrTiO$_3$ at room temperature. This is particularly important in view of the large difference between the experimental values of the dielectric constant of SrTiO$_3$ at 0 K (relative permittivity around 30 000) and at room temperature (relative permittivity around 300): if flexoelectricity scales with permittivity, one would also expect the flexoelectric coefficient at 0 K to be 100 times bigger than at room temperature. On the other hand, the *ab initio* relative dielectric constant of SrTiO$_3$ at 0 K is not as high as the experimental one, because it leaves out the quantum paraelectric oscillations; in fact, the *ab initio* relative permittivity is only 490 [34] which is quite close to the room temperature value of 300, and thus the comparison between the flexoelectric coefficients is legitimate.

The analysis of the results for BaTiO$_3$ is more complicated. On one hand, the calculated flexoelectric

coefficients of BaTiO$_3$ agree in magnitude with the calculations of Maranganti and Sharma [20], and are comparable also to those measured for SrTiO$_3$. However, the longitudinal flexoelectricity of BaTiO$_3$ has not yet been directly measured, so direct comparison with experiment is impossible for this material. Nevertheless, the *transverse* flexoelectric coefficient of BaTiO$_3$ has been measured, and is reported to be of the order of several μC m^{-1} [4], which is several orders of magnitude bigger than our theoretical estimate for the longitudinal one. Such difference clearly demands further discussion.

We begin with the noteworthy discrepancy between the experimental values for BaTiO$_3$ and those of other materials. The experimental flexoelectricity of BaTiO$_3$ is much higher than that of SrTiO$_3$, but also than that of lead-based ferroelectrics [5, 13]. Of course, such differences may be intrinsic, and there is no reason to expect different materials to have the same flexoelectric behavior. In this context, it is worth pointing out that the response of BaTiO$_3$ to uniaxial stress is different from that of SrTiO$_3$. At modest temperatures SrTiO$_3$ can be driven from its cubic structure to tetragonal D$_{4h}$ or rhombohedral D$_{3d}$ by small uniaxial stresses along [111] or [001]. Neither of these phases is polar or ferroelectric [35, 36]. By comparison, uniaxial pressure along [001] drives BaTiO$_3$ from cubic to C$_{4v}$ tetragonal ferroelectric [37]. Therefore, uniaxial stress applied to barium titanate generally gives a polar distortion, whereas in strontium titanate it drives cell-doubling distortions that are non-polar. Since flexoelectric measurements are in essence uniaxial stress experiments—as are, incidentally, our calculations—the different response to uniaxial strain gradients may be consistent with the different response to uniaxial stresses.

Moreover, the differences between the flexoelectricity of BaTiO$_3$ and SrTiO$_3$ are not as large as they appear at first sight. The flexoelectric coefficient is very anisotropic and the

transverse flexoelectric coefficient can be much larger than the longitudinal one. Experimental measurements for $SrTiO_3$, for example, indicate that the transverse flexoelectric coefficient is at least an order of magnitude larger than the longitudinal one [19], and calculations for $BaTiO_3$ also estimate that the transverse flexoelectric coefficient of $BaTiO_3$ is nearly 40 times bigger than the longitudinal one [20]. Furthermore, our flexoelectric coefficients are calculated at 0 K, where the permittivity of $BaTiO_3$ is lower. The relative dielectric constant of $BaTiO_3$ at low temperatures is of the order of 150–200 [38], while at temperatures near the Curie point it is closer to 30 000 [39]. This represents another factor of 100–200 difference, meaning that our calculated longitudinal flexoelectric coefficient, once scaled by the permittivity and the anisotropy, is expected to be of the order of $f_{3333} \sim 2 \ \mu C \ m^{-1}$ near the Curie temperature. This still falls short, albeit only by one order of magnitude, of the nearly 50 $\mu C \ m^{-1}$ reported by Cross for ceramics, the 25 $\mu C \ m^{-1}$ measured by ourselves in single crystals, and the 9 $\mu C \ m^{-1}$ reported by Ma [13].

A further possible cause for the small remaining discrepancy may be crystal symmetry: BTO is rhombohedral at 0 K, but tetragonal and cubic below and above T_c, respectively. Experimentally, the value of the flexoelectric coefficient normalized by the permittivity is known to decrease by a factor of three at the tetragonal–orthorhombic transition [4], and if there were another decrease at the orthorhombic–rhombohedral transition, this would bring the theoretical and measured values completely in line. Testing such hypothesis will require calculating flexoelectricity for symmetries other than the equilibrium one (rhombohedral), or else measuring flexoelectricity in the rhombohedral phase.

On the other hand, it is also possible that the discrepancy is due to the experimental measurements having contributions beyond intrinsic flexoelectricity. One possible extrinsic contribution may arise from piezoelectricity in small polar regions that persist above T_c: in $BaTiO_3$, birefringence experiments have shown that such polar regions can indeed persist far above T_c [40, 41]. Another potential contributor are the surfaces of $BaTiO_3$, which are thought to be polar even in the paraelectric phase [42]. The surface of $BaTiO_3$ has been a subject of intense theoretical and experimental study [43–49], but there is no consensus yet as to how thick the skin layer is. If, as some studies suggest, the surface layer were very thin, the gradients would be very pronounced and surface flexoelectricity could also be an important factor. Also, surface strain gradients can be exacerbated by mechanical polishing and may be detected unambiguously via selection rule violations in infrared and Raman spectroscopy [50]; it is worth investigating whether this happens in $BaTiO_3$. Thickness-dependent flexoelectricity measurements might also help clarify the role of surfaces.

5. Conclusions

We have proposed here a method for calculating the longitudinal flexoelectric coefficient from first principles. Comparison with $SrTiO_3$, the only material for which the longitudinal flexoelectric coefficient has been measured, shows good agreement, suggesting that the method is robust. Direct comparison with $BaTiO_3$ is not possible because only the transverse flexoelectric coefficient has been quoted for this material, but the results nevertheless suggest that there may be an order of magnitude discrepancy between theoretically expected values and the directly measured ones. This calls for two actions: (i) the *ab initio* method proposed here should be modified in order to allow the calculation of transverse flexoelectric coefficients in the cubic phase of $BaTiO_3$ and allow direct comparison with experiments, and (ii) thickness-dependent measurements of flexoelectricity will be performed in single crystals in order to establish whether or not there are extrinsic contributions from the surfaces to the apparent flexoelectricity of this material.

Acknowledgments

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