Photovoltage from ferroelectric domain walls in BiFeO$_3$

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It has been debated for a decade whether the photovoltage in BiFeO$_3$ originates in a bulk photovoltaic effect, a ferroelectric domain-wall effect, or a combination of both. In order to elucidate the role of ferroelectric domain walls for the photovoltaic effect in BiFeO$_3$, we calculated the photovoltage of a single ferroelectric domain wall stemming from photo-generated electron-hole pairs residing at the ferroelectric domain wall, using first-principles calculations based on density-functional theory. We find that at the ferroelectric domain walls the electron-hole pairs form an electric dipole layer resulting in a saw-tooth shaped electronic potential, hence creating a domain-wall driven voltage upon illumination. This domain-wall driven photovoltage in BiFeO$_3$ is smaller than the experimentally measured photovoltage for light intensities up to several tens of mW/cm$^2$, indicating that bulk effects, not domain-wall effects, dominate the photovoltaic effect in BiFeO$_3$ in this intensity range.

Keywords: Condensed Matter & Materials Physics, Ferroelectric Domains, First-principles calculations, DFT+U, Photovoltaic Effect, Exciton, Perovskite

Introduction
It has long been debated whether and to what extent ferroelectric domain walls contribute to the photovoltaic effect in ferroelectric oxides like BaTiO$_3$ and BiFeO$_3$. On the one hand, the so-called bulk photovoltaic effect (BPVE) has been suggested to explain the phenomenon [1-6]. The BPVE is a phenomenological term describing any photovoltaic effect which takes place in the homogeneous interior of the material, as opposed to interface effects. The bulk photovoltaic effect in ferroelectrics such as BiFeO$_3$ and BaTiO$_3$ has been ascribed to non-centrosymmetric scattering or relaxation of electrons and holes after photo-excitation in non-centrosymmetric crystals, resulting in a net shift of charge carriers (“shift current”) [2, 3, 5, 6]. In the case of the BPVE the observed photovoltage characteristically depends on the polarization direction of the incoming light [3]. This angular dependence was indeed observed in the case of BiFeO$_3$, and it was hence concluded that the BPVE is at the origin of the photovoltaic effect in BiFeO$_3$ [7,8].

On the other hand, a domain-wall driven photovoltaic effect (DW-PVE) has been proposed. [9,11] The argument in favour of the DW-PVE is the observation that the lattice polarization in the direction perpendicular to the domain walls is typically locally reduced near the domain wall. It has been suggested that this polarization variation gives rise to internal electrostatic fields at the domain walls. If true, this would mean that ferroelectric domain walls could separate photogenerated charge carriers in the same way as p-n junctions, without the need for n- and p-type doping, and it would be possible to align arbitrarily many such junctions in series and hence add up the individual voltages created by each single junction. However, the DW-PVE theory needs to postulate a local electric polarization. But is it possible to define and determine the electric polarization of an arbitrary section of a crystal? Only then can this local polarization be used to deduce an electric field. Such approach was adopted in previous first-principles studies of voltage drops at ferroelectric domain walls in PbTiO$_3$ [12] and BiFeO$_3$ [9] and yielded voltage drops from 0.02 V to 0.2 V per domain wall were found for the dark state (without illumination). The DW-PVE is independent of the polarization direction of the incoming light.

Some authors [6,13] take the middle ground by assuming that the BPVE and the DW-PVE may exist simultaneously and can be cooperative or antagonistic depending on the system geometry. The argumentation here is based on the observation that on top of the characteristic angular dependence of the BPVE with respect to the polarization of the incoming light, there is an angle-independent offset in the photo-current, which might be ascribed to a DW-PVE originating in an electrostatic field at the ferroelectric domain walls [6], and/or in a locally modified BPVE, caused by the local crystal-structure modifications at the domain walls [13].

Whereas the atomistic structure of ferroelectric domain walls in BiFeO$_3$ is accurately known thanks to electron microscopy [14], an experimental spectroscopy of photo-electrons at ferroelectric domain walls with atomic resolution is to our knowledge not possible today, but is perfectly within reach of first-principles calculations based on density-functional theory (DFT). Optical excitations and the spatial distributions of the photo-excited charge carriers in molecules and solids are nowadays routinely investigated by means of many-body perturbation theory [15-18]. In the case of ferroelectric domain walls such studies are hampered by the relatively big system size that a domain wall represents, however there exist approximations which make it possible to investigate even such systems with a favorable balance between accuracy and computational cost. Such an approximation is the excitonic Delta-self-consistent-field (ΔSCF) method, which has been shown to yield more than qualitative agreement with highly accurate many-body methods [19], but can be performed at the same computational cost as a ground-state calculation with DFT. The excitonic ΔSCF approach was applied before to study excitons in various systems, including organic dyes [20], polymers [19,21] and surfaces [22], systems which like ours are too large to apply many-body perturbation theory such as the Bethe-Salpeter equation or time-dependent density-functional theory. Here we use the excitonic ΔSCF method to directly determine the magnitude of the domain-wall driven photovoltaic effect in BiFeO$_3$, as given by
the electronic potential induced by excitons localized at the domain walls.

Methods We focus on the 71° and the 109° domain wall, for which the direction of the ferroelectric polarization in adjacent domains differs by about 71° and by 109°, respectively. In rhombohedral perovskites like BiFeO$_3$ there exists also a 180° domain wall, however due to its symmetry it should be photovoltaically inactive, and hence we do not consider it here. The DFT calculations were performed with the VASP code [23], using the Projector-Augmented Wave (PAW) method and pseudopotentials with 5 (Bi), 16 (Fe), and 6 (O) valence electrons, respectively. We employed the local-spin density approximation (LSDA), and corrected the 3$d$ states of Fe with a Hubbard-$U$ term of 5.3 eV following Dudarev’s scheme [24]. The $U$ value for Fe was taken from the materials project [25] and it is optimized for oxide formation energies, but also yields band gaps close to experiments. The reciprocal space was sampled with $2 \times 3 \times 3$ $k$-points for the 71° wall and with $2 \times 5 \times 5$ $k$-points for the 109° wall. Plane-wave basis functions with energies up to 520 eV were used. We employed a supercell approach with periodic boundary conditions, such that each supercell contained 120 atoms and two domain walls. Both the atomic positions and cell parameters were allowed to relax until the energy difference between subsequent ionic relaxation steps fell below 0.1 meV. Excitons were modeled with the excitonic $\Delta$SCF method [26], namely by setting the occupation numbers of the valence-band states to $(N - N_X)$, where $N$ is the number of electrons and $N_X$ is the number of excitons in the supercell, and that of the conduction bands to $N_X$ in every iteration step of the electronic self-consistency cycle, using the same density functional for minimizing the energy as in a ground-state calculation. The structures were optimized in the presence of the exciton when considering excitonic polaron states. The excitonic $\Delta$SCF method is suitable for exploring low-lying excited states, whereas access to higher-lying excited states such as Rydberg states can be obtained using constrained DFT [26, 27] or by maximizing the similarity of the excited-state orbitals with reference orbitals [28, 29].

Results and discussion Depending on the exciton density, we observe two different types of excitons, as depicted in Fig. 1. For low exciton densities, we find a large exciton with photo-electrons and -holes weakly localized on opposite sides of the domain wall resulting in an excitonic dipole moment. At high exciton densities, we find instead a small, almost concentric exciton polaron (a self-trapped exciton) without almost any dipole moment. Figure 2 shows the densities of excess electrons and holes for different numbers of excitons in the 120-atom supercell, and the excitation energy per exciton of the large exciton and the small exciton. There is a critical exciton density above which the large exciton polaron transforms into a small exciton polaron (above which the formation energy of the small exciton polaron becomes lower than that of the large exciton polaron), and a coexistence region. Since only the large exciton configuration will lead to a sizeable photovoltage, we determine next under which experimental conditions the large exciton forms. In Ref. 30 it was found that the photocurrent in BiFeO$_3$ follows a rate equation

$$n = g - n/\tau,$$

where $n$ is the photo-carrier density, $g$ is the photo-carrier generation rate, and $\tau \approx 75 \mu s$ is the photo-carrier lifetime. Here we adopt the same rate equation to describe the exciton density $n_X$, which in the steady state is given by

$$n_X = g \tau = \frac{I_{\text{light}}(1 - R)\tau}{E_{\text{photon}}d_{\text{film}}},$$

where $I_{\text{light}}$ is the intensity of the light in W/cm$^2$, $d_{\text{film}}=100$ nm is the thickness of the experimentally studied films in Refs. 7 and 11, $E_{\text{photon}}=3.06$ eV is the photon energy of the laser used in the experiment in Ref. 7 and $R \approx 0.27$ is the reflectivity calculated at this photon energy from first-principles.

The resulting critical light intensity and domain-wall spacing for which the small exciton polaron begins to form is depicted in Fig. 3. In the case of natural sunlight and typical domain-wall spacings of a few hundred nanometers, the large exciton forms, which should give rise to a photovoltage, whereas in the case of a thousand-fold concentrated sunlight, such as in a concentrator solar-cell setup, we expect the small exciton polaron, which should contribute less to the photovoltage, if at all. The small exciton polaron might be detectable with photoluminescence spectroscopy.

In the following, we will consider moderate light intensities, at which we expect the large exciton, and use the saw-tooth potential of the large exciton (the Kohn-Sham potential from a one-shot excitonic $\Delta$SCF calculation), depicted in Fig. 4, to estimate the maximum photovoltage generated by a single domain wall. For small exciton densities, where our numerical accuracy deteriorates, we extrapolate the photovoltage dependence on the exciton density by a power law fitted...
FIG. 1: Excitonic phase diagram. The solid blue line indicates the transition between a large exciton ("X") and a small exciton, the dashed blue lines mark the boundaries of a coexistence region. Orange vertical bars mark the intensity of sunlight and thousand-fold concentrated sunlight above the band gap of BiFeO$_3$, and the grey horizontal bar marks a range of typical domain-wall spacings found in the experimental literature.

FIG. 2: (Color online) Top: Densities of excess electron and hole as a function of the number of excitons (X) in the 120-atom supercell with the 71° domain wall. The strong variations near atomic nuclei were smoothened by a sliding-window average. Solid and dashed lines mark small and large polarons, respectively. Bottom: Excitation energies per exciton of the small (small filled circles) and the large exciton (large empty circles). The critical density $n_{X}^{\text{crit}}$ at which the large exciton polaron transforms into a small exciton polaron and the coexistence region are marked by vertical solid and dashed lines, respectively. The lower boundary of the coexistence region in the graph is an estimated upper limit.

to our high-density data,

$$\Delta V^{\text{DW}}(n_X) = \Delta V^{\text{DW}}(n_X^{\text{ref}}) \left( \frac{n_X}{n_X^{\text{ref}}} \right)^p,$$

where $n_X^{\text{ref}}$ is the reference planar exciton density for which we obtained the potential contribution $\Delta V^{\text{DW}}$. The relation between exciton density and light intensity is the same as in Eq. (2), using the parameters of the experimental measurement of the photovoltage in Ref. [11] ($E_{\text{photon}} = 3.31$ eV, $R = 0.25$, $d_{\text{DW}}=140$ nm). The fit yields exponents $p = 0.73$ for the 71° wall and $p = 0.69$ for the 109° wall. The resulting photovoltage contribution per domain wall, together with the experimental results from Ref. [11] are depicted in Fig. 5. The experimental conditions are well inside the range in which the large exciton forms (marked by the blue solid line), for which our approach is valid. It should be noted that our approach leads to rather overestimated photovoltages, as we neglect the limited diffusion length of the photocarriers and instead assume that all of them reach the domain walls, and we consider the instantaneous voltage response only, neglecting the screening effect of the lattice. In spite of this overestimation of the photovoltage, the calculated photovoltage remains considerably below the experimentally measured one up to light intensities of tenths of mW/cm$^2$, indicating that the DW-PVE cannot account for the major part of the photovoltage in BiFeO$_3$ in this intensity range. Only for the highest light intensities used in experiment does our calculated voltage approach the measured one, however in this region we expect small exciton polaron formation to set in, which would reduce the photovoltage. This effect is not included in our calculation. The domain-wall driven photovoltage can be ex-
FIG. 4: (Color online) Induced electronic potential $\Delta V$ for an exciton density $n_{\text{ref}}^X = 0.1$ $X$ per supercell. Top: $71^\circ$, bottom: $109^\circ$ domain wall. Gray bars and arrows schematically indicate ferroelectric domain walls and polarization direction. Because of the periodic boundary conditions adopted in our calculations, there is no net voltage, corresponding to short-circuit conditions (solid line). If we remove periodic-boundary effects, we obtain open-circuit conditions (dashed line). $\Delta V_{\text{DW}}$ is the photovoltage contribution per domain wall. The strong variations near atomic nuclei were smoothened by a sliding-window average.

FIG. 5: (Color online) Photovoltage per domain wall as calculated here for the $71^\circ$ (brown filled circles) and the $109^\circ$ domain wall (green open circles) and as measured by Seidel et al. for the $71^\circ$ domain wall (empty squares) [11]. The solid lines are extrapolations (fits) with a power law according to Eq. [3].

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