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Theory of Transport in Ferroelectric Capacitors

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The spontaneous order of electric and magnetic dipoles in ferroelectrics and ferromagnets even at high temperatures is both fascinating and useful. Transport of magnetism in the form of spin currents is vigorously studied in spintronics, but the polarization current of the ferroelectric order has escaped attention. We therefore present a time-dependent diffusion theory for heat and polarization transport in a planar ferroelectric capacitor with parameters derived from a one-dimensional phonon model. We predict steady-state Seebeck and transient Peltier effects that await experimental discovery.

Ferromagnetism and ferroelectricity describe the order of magnetic and electric dipoles that spontaneously forms often far above room temperature and have much in common [1]. The robustness of the order and the associated stray magnetic and electric fields give rise to numerous technological applications that affect our daily life. The physics appears to be very different, however. The Amperian electric (Gilbertian magnetic) dipoles break (conserve) inversion symmetry, but conserve (break) time-reversal symmetry. Furthermore, the static electric dipolar interaction is much larger than the magnetic one. According to the Bohr-van Leeuwen theorem, magnetism is a quantum effect, while ferroelectricity can exist in the classical realm. Nevertheless, the phenomenology of these material classes displays close analogies. The dipolar order is staggered in antiferromagnets as well as antiferroelectrics. The electrocaloric (magnetocaloric) effect is based on the dependence of the entropy of the electric (magnetic) dipolar ensembles as a function of applied electric (magnetic) field and temperature [2]. Both magneto- as well as electrocaloric heat pumps appear to be close to the market.

"Spintronics" addresses transport in magnetic structures and devices [3]. Not only magnetic metals, but also electrically insulating magnets are important spintronic materials because spin waves carry angular momentum or spin currents that can be excited and detected by heavy metal contacts [4]. Spin caloritronics is the study of coupled spin, heat and charge currents, covering the spin Seebeck and spin Peltier effects [5, 6]. Surprisingly, only very few studies address transport in ferroelectrics (FEs). A thermopolarization [7–9] and dielectric Peltier effect [10, 11] have been reported. However, the theory underlying these studies inappropriately mixes electrocaloric/pyroelectric effects, i.e. adiabatic transients between equilibrium states, with transport or caloritronic, i.e., genuine non-equilibrium phenomena.

In the Letter, we take the first steps in the equivalent to spintronics in ferroelectrics by reporting a theory of polarization and heat currents in electrically insulating ordered FEs in response to electric field and temperature gradients. The predicted polarization Seebeck and Peltier effects turn out to be observable already for the most basic, yet experimentally relevant device, i.e. a slab of an FE between electric contacts (see Fig. 1), for which we solve the time-dependent diffusion equation for the polarization accumulation in the FE with boundary conditions to metallic reservoirs. We estimate the parameters by solving the Boltzmann equation for a one-dimensional chain of elastically coupled dipoles, which is a microscopic model for the FE excitations at temperatures sufficiently below the phase transition. The analogies and differences with magnon transport are illuminating [12, 13].

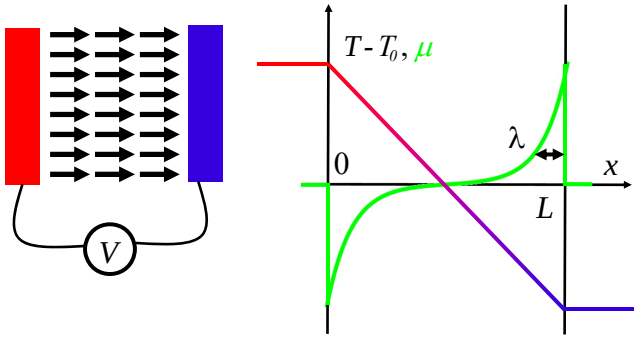

FIG. 1. (Left) Planar capacitor of an ordered ferroelectric with thickness L between metal contacts connected by a voltmeter. (Right) An applied temperature bias generates a steady-state polarization accumulation (or chemical potential) distribution μ. The green line illustrates the case of two opaque interfaces with relaxation length λ (see text) .

Linear response - We consider an FE with metal contacts in a planar configuration with polarization density $p(x)$ normal to the interfaces, which interacts with an

electric field $E(x)$ as

$$H = -\int p\left(x\right) E\left(x\right) dx. \tag{1}$$

Temperature (∂T) and electric field (∂E) gradients generate heat j_q and polarization j_p current densities. Here j_p denotes the non-equilibrium transport of electrical polarization in real space and should not be confused with the dielectric displacement current, i.e. the time derivative of the polarization. In the linear response regime, "currents" and "forces" are related by a matrix of material and device-dependent transport coefficients [14, 15]. The caloritronic relations can be summarized by a 2×2 linear response matrix

$$\left(\begin{array}{c} j_p \\ j_q \end{array} \right) = \sigma \left(\begin{array}{cc} 1 & S \\ \Pi & \kappa/\sigma \end{array} \right) \left(\begin{array}{c} \partial E \\ -\partial T \end{array} \right), \tag{2}$$

where σ (κ) is the polarization (thermal) conductivity with units m/Ω (W/m/K), while S (Π) is the ferroelectric Seebeck (Peltier) coefficient with units V/K/m (V/m). The dissipation rate $\dot{f} = j_p \partial E + j_q \partial T/T$ implies the Onsager-Kelvin relation $\Pi = TS$. For a mono-domain simple FE all transport coefficients should be positive.

The electrocaloric (and pyroelectric) properties are governed by the temperature and field dependent thermal equilibrium polarization $p_0\left(E,T\right)$ and heat/energy $q_0\left(E,T\right)$ densities with susceptibilities $\chi_E = \left(\partial p_0/\partial E\right)_T$ and $\chi_T = \left(\partial p_0/\partial T\right)_E$.

Metallic contacts efficiently screen the surface charges. When shorted, the electric field in the FE vanishes except for small corrections due to a finite screening length [17]. A constant applied voltage $\triangle V_{\text{ext}}$ generates an electric field $E_{\text{ext}} = \triangle V_{\text{ext}}/L$, but since $\partial E_{\text{ext}} = 0$ there can be no DC Peltier effect. A temperature difference $\triangle T_{\text{ext}}$ between the contacts generates a gradient $\partial T_{\text{ext}} = \triangle T_{\text{ext}}/L$. The polarization current into a metal contact is dissipated quickly without measurable effects. The principle observables are the electric field-induced Peltier heat current and the Seebeck thermovoltage over the contacts induced by a polarization change

$$\triangle V = -\int \frac{p - p_0}{\epsilon} dx, \tag{3}$$

where ϵ is the dielectric constant.

Diffusion - The conservation relation for the FE polarization reads

$$\partial j_p = -\dot{p} - \frac{p - p_0}{\tau} \tag{4}$$

in terms of the relaxation time τ. A similar equation holds for the heat accumulation, but we assume from the outset that it relaxes much faster than that of the polarization, so the local temperature instantaneously adapts to the external one. We also assume that thermalization of the non-equilibrium ferroelectric order can be modelled by an equilibrium distribution with a local temperature $T_{\text{ext}}\left(x,t\right)$ and a non-equilibrium chemical potential $\mu\left(x,t\right)$ [12]. It is convenient to define $\mu_{\text{tot}} = \mu - PE_{\text{ext}}$, where P is the electric dipole of the unit cell such that the driving force in Eq. (2) $E \to -\mu_{\text{tot}}/P$. With $p - p_0 = \chi_E \mu/P + \chi_T \left(T - T_0\right)$, we arrive at the diffusion equation for the non-equilibrium chemical potential

$$\partial^2 \mu - \frac{1}{\lambda^2}\mu = \frac{\tau}{\lambda^2}\left(\dot{\mu}_{\text{tot}} + \frac{P\chi_T}{\chi_E}\dot{T}_{\text{ext}}\right) \tag{5}$$

with diffusion length $\lambda = \sqrt{\sigma\tau/\chi_E}$. In frequency ($\omega$) space

$$\partial^2 \mu - \frac{\mu}{\bar{\lambda}^2} = -\frac{i\omega\tau}{\lambda^2}\dot{F}_{\text{ext}}\left(x,\omega\right) \tag{6}$$

where $F_{\text{ext}} = -PE_{\text{ext}} + \chi_T T_{\text{ext}}/\chi_E$ and $\lambda^2/\bar{\lambda}^2 = 1 - i\omega\tau$. For a capacitor with contacts at $x_1 = 0$, $x_2 = L$, using $\partial^2 F_{\text{ext}} = 0$ and short diffusion lengths $\lambda \ll L$,

$$\begin{aligned} \mu\left(x,\omega\right) = {} & A\left(\omega\right) e^{-x/\bar{\lambda}} + B\left(\omega\right) e^{-(x-L)/\bar{\lambda}} \\ & + \frac{i\omega\tau}{1 - i\omega\tau} F_{\text{ext}}\left(x,\omega\right), \end{aligned} \tag{7}$$

Interfaces - The boundary conditions to the contacts fix the integration constants A and B. The interface transport coefficients obey an Onsager relation similar to Eq. (2). Demanding continuity of the polarization current, the boundary conditions for the chemical potential are governed by an interface conductance G

$$G\mu\left(0^+\right) = \sigma\partial\mu\left(0^+\right);\; G\mu\left(L^-\right) = -\sigma\partial\mu\left(L^-\right). \tag{8}$$

We focus below on two limiting cases. A good metal contact efficiently screens the polarization dynamics and suppresses the chemical potential at the interface. This is the transparent interface limit $G \gg \sigma/\lambda$. The opposite limit of an opaque interface with $G \ll \sigma/\lambda$ represents, e.g., a contact with a thin non-FE spacer between FE and the metal.

Solutions - Close to the left interface

$$\begin{aligned} \mu\left(x,\omega\right) = {} & \frac{\lambda}{\frac{\lambda G}{\sigma} + \sqrt{1 - i\omega\tau}} \\ & + \frac{i\omega\tau}{1 - i\omega\tau}\left[\partial F_{\text{ext}}\left(\omega\right) - \frac{G}{\sigma} F_{\text{ext}}\left(0,\omega\right)\right] \end{aligned} \tag{9}$$

In the DC limit $\omega \to 0$

$$\mu_{\text{DC}}\left(x\right) = \frac{\lambda}{\frac{\lambda G}{\sigma} + 1} e^{-x/\lambda} PS\partial T_{\text{ext}} \tag{10}$$

The thermovoltage generated by a temperature difference

$$\triangle V_{\text{DC}} = -\frac{\lambda}{\frac{\lambda G}{\sigma} + 1}\frac{\chi_E}{\epsilon}\frac{\lambda}{L} S \triangle T_{\text{ext}} \tag{11}$$

is maximized for an opaque interface $G/\sigma \to 0$. This voltage can be observed when the opposite interface is transparent, i.e. does not accumulate any polarization. In the symmetric capacitor sketched in Figure 1, the accumulations at the interfaces have equal moduli but opposite sign and the thermovoltage vanishes. The theoretically possible maximal thermovoltage in the weakly dissipative limit ($L \ll \lambda$) for one transparent and one opaque interface is $\triangle V_{\max} = -\chi_E L S \triangle T_{\rm ext}/(2\epsilon)$, which can be compared with the pyroelectric voltage $-\chi_T L \triangle \bar{T}/\epsilon$ generated by a global temperature change $\triangle \bar{T}$. When shorting the contacts the charged capacitor generates a charge current pulse on the scale of the RC time of the circuit.

At finite frequencies, the length and time scales λ and τ govern the dynamics. We consider the transients generated by switching on the external perturbation $F_{\rm ext} = F_{\rm ext}^{(\Theta)}\Theta(t)$, where Θ is the step function, on a time scale faster than τ. The Fourier transform back to the time domain can be carried out by contour integration.

The transient polarization accumulation in the FE at a transparent (left) interface generated by an electric field pulse reads

$$\mu(x, t>0) = -e^{-t/\tau} P E_{\rm ext}^{(\Theta)} \,{\rm erf}\left(\frac{1}{2}\sqrt{\frac{\tau}{t}}\frac{x}{\lambda}\right). \qquad (12)$$

We recover the pure electrocaloric term in the bulk of the FE $\mu(x \gg \lambda, t>0) = -e^{-t/\tau} P E_{\rm ext}^{(\Theta)}$, which dominates the observable thermovoltage. The polarization current in the absence of a temperature gradient is caused by the leakage of the electrocaloric accumulation into the contact, which on the left side assumes the form

$$j_p(x, t>0) = \sigma\sqrt{\frac{\tau}{\pi t}} e^{-\frac{t}{\tau} - \frac{\tau}{t}\left(\frac{x}{2\lambda}\right)^2} \frac{E_{\rm ext}^{(\Theta)}}{\lambda}, \qquad (13)$$

while that for the right contact has the opposite sign. The associated Peltier heat current $j_q = \Pi j_p$ cools the FE and heats the contacts or *vice versa,* with a possible interface contribution.

In the opaque interface limit

$$\mu(x, t>0) = PS\lambda\partial T_{\rm ext}^{\Theta}\left(e^{-x/\lambda} - \frac{1}{2}\left[e^{-x/\lambda}{\rm erfc}\left(\sqrt{\frac{t}{\tau}} - \frac{x}{2\lambda}\sqrt{\frac{\tau}{t}}\right) + e^{x/\lambda}{\rm erfc}\left(\sqrt{\frac{t}{\tau}} + \frac{x}{2\lambda}\sqrt{\frac{\tau}{t}}\right)\right]\right)$$
$$+ e^{-t/\tau}\left[-F_{\rm ext}^{(\Theta)} + \frac{P\chi_T}{\chi_E}\partial T_{\rm ext}^{(\Theta)}\left(x\,{\rm erf}\left(\frac{1}{2}\sqrt{\frac{\tau}{t}}\frac{x}{\lambda}\right) + \frac{2\lambda}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}}e^{-\frac{\tau_E}{t}\left(\frac{x}{2\lambda}\right)^2}\right)\right] \qquad (14)$$

The polarization current vanishes at the interface $x = 0$, but

$$\mu(0, t>0) = PS\lambda\,{\rm erf}\left(\sqrt{t/\tau}\right)\partial T_{\rm ext}^{(\Theta)} +$$
$$e^{-t/\tau}\left[-F_{\rm ext}^{(\Theta)}(0) + P\frac{\chi_T}{\chi_E}\partial T_{\rm ext}^{(\Theta)}\frac{2\lambda}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}}\right] \qquad (15)$$

We recognize a Seebeck contribution caused by the build-up of a polarization accumulation/depletion at the interface that approaches the DC limit Eq. (10) for long times. The second term is purely electrocaloric and corrected for diffusion by the third term.

Phonon model - The phenomenological theory does require assumptions about the nature of the ferroelectric phase transition, which may be, e.g., of the "order-disorder" or "displacive" type. The magnitude of the caloritronic parameters σ and Π can be either fitted to experimental results or calculated from a microscopic model. In the absence of both, we derive here estimates by a simple model of one-dimensional diatomic chains at temperatures below the phase transition that generates a permanent electric dipole $P = \delta Q$ in each unit cell, where δ is the deformation and Q the ionic charge. At finite temperatures the polarization is affected by transverse phonons (not to be confused with the soft phonons that trigger a displacive phase transition) with maximum frequency $\omega_{\rm op} = 2\sqrt{C/M}$, where M is the ionic mass and C the force constant. We introduce here the "ferron" model that the thermal fluctuations leave P invariant, but reduce its projection along the FE order. This is a valid approximation when the intra-dipole longitudinal oscillation frequency is sufficiently higher than $\omega_{\rm op}$ and the inter-dipole frequency. At temperatures $k_B T \gg \hbar\omega_{\rm op}$ the Boltzmann equation for a constant scattering relaxation time $\tau_r \ll \tau$ then leads to a Peltier coefficient

$$\Pi = \left.\frac{J_q}{J_p}\right|_{\partial T=0} = \frac{C\delta^2}{P}, \qquad (16)$$

and conductivities

$$\sigma = \frac{\tau_r}{\Pi^2}\frac{\omega_{\rm op}^2}{8a}k_B T, \qquad (17)$$

$$\kappa = \sigma\Pi^2/T, \qquad (18)$$

where a is the lattice constant. In this model, the elec-

trocaloric properties also depend on the Peltier coefficient

$$\chi_E = \frac{k_B T}{a^3 \Pi^2};\ \chi_T = -\frac{k_B}{a^3 \Pi}\left(1 - \frac{E}{\Pi}\right). \tag{19}$$

A stiffer material increases the heat relative to the polarization current, suppressing polarization caloric and enhancing caloritronic effects. The figure of merit

$$ZT = (\sigma/\kappa)\left(\Pi^2/T\right) = 1 \tag{20}$$

does not depend on the model parameters and temperature (even when $k_B T \not> \hbar\omega_{\rm op}$).

Estimates - We choose room-temperature material constants $\omega_{\rm op} = 5\,\mathrm{THz}$, $a = 0.4\,\mathrm{nm}$, $P = 2\times10^{-29}\,\mathrm{Cm}$, $\delta = 0.03\,\mathrm{nm}$, $C = 25\,\mathrm{J/m^2}$, $\tau_r = 1\,\mathrm{ps}$, and $\tau = 1\,\mathrm{ns}$ lead to $\Pi = 10\,\mathrm{MV/cm}$, $\chi_E = 7\times10^{-11}\,\mathrm{C/(Vm)}$, $\chi_T = -2\times10^{-4}\,\mathrm{C/(Km^2)}$, $\kappa = 4\,\mathrm{W/(Km)}$, $\sigma = 10^{-15}\,\mathrm{m/\Omega}$, $\lambda = 130\,\mathrm{nm}$, and $\epsilon/\epsilon_0 = 2000$ in terms of the vacuum dielectric constant ϵ_0. These numbers are rather arbitrary, but close to the parameters of displacive FEs such as barium titanate. The predicted DC thermovoltage induced by a temperature gradient of $\partial T = 10\ \mathrm{K}/\mu\mathrm{m}$ at an opaque interface is then $\triangle V = 2\,\mathrm{mV}$. The integrated heat flow through a transparent interface $\int j_p\,(0,t)\,dt$ excited by an electric field pulse of $E^{(\Theta)}_{\rm ext} = 1\,\mathrm{MV/cm}$ is $9\,\mathrm{J/m^2}$. Because of the uncertainties in the parameters and simplicity of the model these numbers should be taken with a grain of salt.

Summary - We predict polarization caloritronic effects in planar capacitors filled with an electrically insulating ferroelectric that may interfere with normal operation or be used for energy applications and thermal management. The present model can be extended into many directions, such as Kelvin probe force microscopy of textured ferroelectric surfaces [18], polar metals [19], and multiferroics [20]. We focus here on polarization relaxation lengths that are short compared to the sample dimensions, but this is not an essential approximation. For example, large thermovoltages might be generated in boron nitride bilayers with a switchable ferroelectric order [21].

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