Why is the electrocaloric effect so small in ferroelectrics?

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Ferroelectrics are attractive candidate materials for environmentally friendly solid state refrigeration free of greenhouse gases. Their thermal response upon variations of external electric fields is largest in the vicinity of their phase transitions, which may occur near room temperature. The magnitude of the effect, however, is too small for useful cooling applications even when they are driven close to dielectric breakdown. Insight from microscopic theory is therefore needed to characterize materials and provide guiding principles to search for new ones with enhanced electrocaloric performance. Here, we derive from well-known microscopic models of ferroelectricity meaningful figures of merit which provide insight into the relation between the strength of the effect and the characteristic interactions of ferroelectrics such as dipole forces. We find that the long range nature of these interactions results in a small effect. A strategy is proposed to make it larger by shortening the correlation lengths of fluctuations of polarization.

The thermal changes that occur in ferroelectric (FE) materials upon the application or removal of electric fields are known as the electrocaloric effect (ECE).\textsuperscript{1–5} The effect was first studied in Rochelle salt in 1930\textsuperscript{6} and it’s the electric analogue of the magnetocaloric effect, which is commonly used to reach temperatures in the milliKelvin range. The ECE is the result of entropy variations with polarization, e.g., isothermal polarization of a ferroelectric reduces its entropy while depolarization increases it. It is parametrized by isothermal changes in entropy $\Delta S$ and adiabatic changes in temperature $\Delta T$ and it is strongest near the ferroelectric transition.

Since the phase transitions occur near room temperature in many FEs, the potential for using the ECE for cooling applications is huge: it could provide an alternative to standard refrigeration technologies based on the vapor-compression method in which the running substances are greenhouse gases such as freon and hydrochlorofluorocarbons;\textsuperscript{7} replace the widely used but inefficient small thermoelectric cooling devices such as Peltier coolers;\textsuperscript{1} and lead to energy harvesting applications.\textsuperscript{8} Moreover, developing cooling prototypes based on the ECE such as multilayer capacitors\textsuperscript{9} and electrocaloric oscillatory refrigeration\textsuperscript{10} may have several advantages over those based on the more studied magnetocaloric effect as the magnetic materials of interest require expensive rare-earth elements and large magnetic fields, while many FEs are ceramics or polymers, which are cheap and can be driven with electric fields that are easy to generate.

Though promising, a major challenge is that the magnitude of the ECE remains too small for useful applications: in bulk FEs, $\Delta T$ is usually less than a few milliKelvin per Volt and $\Delta S$ is usually a fraction of a J K$^{-1}$mol$^{-1}$.\textsuperscript{1} FE thin films exhibit ECEs of about an order of magnitude larger than their bulk counterparts as they can withstand larger breakdown electric fields.\textsuperscript{11} Thin films, however, have small cooling power because of their small heat capacities. Ferroelectric polymers have also received considerable attention with ECEs comparable to those of thin films, though they must be driven at larger electric fields than those of thin films.\textsuperscript{12}

In the light of these challenges, it has been recently pointed out that insight from microscopic theory into the ECE may contribute to characterize known materials and provide guiding principles to search for new ones with enhanced electrocaloric performance.\textsuperscript{1} Here, we provide such insight by deriving meaningful figures of merit from well-known microscopic models of ferroelectricity. Our figure of merit allow us to set trends across different classes of FE materials (order-disorder and displacive) and provides insight into the relation between the magnitude of the ECE and the characteristic interactions of FEs (e.g. dipolar and strain). We find that the long-range nature of these interactions produces trade-offs in the ECE: while they can give rise to high transition temperatures (i.e., comparable to room temperature), they concomitantly give rise to long correlation lengths of polarization at finite electric fields, which, as we show here, result in a small effect. We make contact with well-known results derived from Ginzburg-Landau (GL) theory\textsuperscript{13} and those from heuristic arguments.\textsuperscript{14} Based on these findings, we then study the effects of compositional disorder. The purpose of this is twofold: to propose a strategy to increase the magnitude of the ECE and to model the ECE of so-called relaxor ferroelectrics - a widely studied class of electrocaloric materials with diffuse phase transitions that could provide a broad temperature range of operation in a cooling device.\textsuperscript{14–25} We find that the commonly observed broad peak in the ECE of relaxors is expected in any ferroelectric that is deep in the supercritical region of their phase diagram. Our results also bring into question the common practice of defining the electrocaloric strength of a material as the ratio of the entropy or temperature changes over the change in applied electric field.\textsuperscript{1,3}

To illustrate the ideas presented above, we adhere to a simple microscopic model for displacive ferroelectrics...
with quenched random electric fields. Such compositional disorder is typical of relaxor ferroelectrics such as the prototype PbMg\(_{1/3}\)Nb\(_{2/3}\)O\(_3\) (PMN) and it arises from the different charge valencies and disordered location of the Mg\(^{+2}\) and Nb\(^{+5}\) ions. In the absence of disorder, it is a standard minimal model of ferroelectricity. With disorder, the model gives a good starting point for the description of the static dielectric properties of relaxors.

In calculating the ECE in the presence of compositional disorder, it is important to recall that Maxwell relations are not applicable. Maxwell relations are usually invoked in ferroelectrics to indirectly determine, for instance, adiabatic changes in temperature \(\Delta T\) from the variations of the polarization with respect to temperature. Pure ferroelectrics are in thermodynamic equilibrium, thus Maxwell relations hold. Disordered ferroelectrics are not in thermodynamic equilibrium, thus Maxwell’s relations do not apply. This is supported by the recent experimental observation that direct measurements of \(\Delta T\) in solutions of the relaxor ferroelectric polymer PVDF-TrFE-CFE with PVDF-CTFE were significantly larger than those estimated from their polarization curves. Another difficulty is that GL theory fails for relaxors. GL theory is applicable away from the region of critical fluctuations, but Maxwell relations do not apply. This region is narrow. In relaxors, on the other hand, GL theory is not expected to hold as the region of critical fluctuations is broad. We overcome both of these difficulties by calculating the ECE directly from the entropy function (see supplement).

We first consider the case without compositional disorder. In the absence of disorder and no applied electric field, the model gives a second-order paraelectric-to-ferroelectric phase transition at a transition temperature \(T_c\). Consider an isothermal change in entropy \(\Delta S(T, E_0)\) near \(T_c^0\) that results from a change in electric field \(\Delta E_0 = 0 \rightarrow E_0\). Within a mean field approximation, we find that

\[
\frac{|\Delta S(T, E_0)|}{Nk_B} = (2\pi\zeta a^2/3) \left[ \xi^{-2}(T, E_0) - \xi^{-2}(T, 0) \right].
\]

(1)
the lattice structure, \(a\) is the lattice constant and \(N\) is the number of lattice sites.\(^{26}\) \(\xi(T, E_0)\) is the correlation length of the exponentially decaying fluctuations of polarization at the field \(E_0\) and temperature \(T\).\(^{13}\) It is given by the (soft) frequency of the transverse optic phonon mode\(^{26}\) and it diverges as \(\xi(0, T) \propto (|T - T_c|)^{-1/2}\) at the onset of the FE transition.\(^{13}\) A similar relation is derived for the adiabatic changes in temperature \(\Delta T(T_1, E_0) = T_2 - T_1\),

\[
\frac{\Delta T(T_1, E_0)}{T_1} = \frac{\pi a^2}{3} [\xi^{-2}(T_2) - \xi^{-2}(0, T_1)].
\]

Equations (1) and (2) relate the ECE to the correlation length of a ferroelectric. We make contact with known results by noting that near the FE transition, \(\xi(T, E_0)/a^{-2} = (\xi(T, 0)/a)^{-2} \approx (\kappa_B n)^{-1} P_s^2(T, E_0)/C_{C_W}\) in Eqs. (1), which gives the standard results from GL theory,\(^{13}\) and similar form to those derived from heuristic arguments.\(^{14}\) \(P_s(T, E_0)\) is the polarization at temperature \(T\) and at field \(E_0\), \(C_{C_W}\) is the Curie-Wiess constant, and \(n = N/V\) is the number of lattice points per unit volume \(V\). At the phase transition, \(\Delta S(T_c, E_0)\) and \(\Delta T(T_c, E_0)\) of Eqs. (1) and (2) peak as the correlation length at zero field diverges \((\xi(T_c, 0) = \infty)\) and their magnitude depends on that at finite fields. For ferroelectrics, it is well-known that these tend to be large due to the long-range nature of the dipole and strain interactions.\(^{13}\)

We now derive our figure of merit. By evaluating the correlation length at the critical temperature \((\xi^{-2}(E_0, T^0_c) \propto (T^0_c/C_{C_W})^{1/3} (E_0/P_s^2)^{2/3})\) in Eqs. (1) and (2), we obtain the magnitude of the ECE in terms of dielectric properties of a FE,

\[
\frac{\Delta T(T^0_c, E_0)}{T^0_c} \approx \frac{\Delta S(T^0_c)}{N\kappa_B/2} \propto \left(\frac{T^0_c}{C_{C_W}}\right)^{1/3} \left(\frac{E_0}{P_s^2}\right)^{2/3},
\]

where \(P_s^2 = P_s(0, 0)\) is the saturated polarization at zero field. The coefficient of proportionality is a dimensionless number \((81/(4\pi))^{2/3} \approx 1.7\). Eq. (3) is our figure of merit. The available data confirm the prediction of our simple model. Figure 1 shows the field dependence of \(\Delta T\) near the ferroelectric transition in triglycine sulphate (NH\(_2\)CH2COOH)\(_3\)·H\(_2\)SO\(_4\)), or TGS for simplicity. The adiabatic changes in temperature are well described by the non-linear relation of Eq. (3) (though TGS is a ferroelectric of the order-disorder type, it is straightforward to show that its ECE scales with the electric field according to Eq. (3)). Similar scaling
laws have been observed in the magnetocaloric effect. The non-linearity in \(E_0\) suggests that it is not meaningful to define \(\Delta S/\Delta E_0\) or \(\Delta T/\Delta E_0\) as the electrocaloric strength of an electrocaloric material when \(\Delta S\) and \(\Delta T\) are measured near or at the transition temperature.\(^1\)

From Eq. (3) and data from the literature,\(^9\) we calculate our figure of merit for several FE materials. The results are shown in Figure 2. Our model predicts a clear trend: order-disorder FE should display larger ECE than that of the displacive type. This is a consequence of the shorter correlation lengths that the former type generally display compared to those of the latter type (order-disorder Curie-Weiss constants are typically about two orders of magnitude smaller than those of displacive FE). An exception to this rule may exist, however, in the ultraweak displacive FE such as tris-sarcosine calcium chloride (TSCC). Our predicted figure of merit is an order of magnitude larger than any of the FE considered here as a result of their exceptionally small Curie-Weiss constants and spontaneous polarization (which result in shorter correlation lengths).\(^3\) When Eq. (3) is contrasted to experiments,\(^4\) there are clear discrepancies which we attribute to the mixed order-disorder and displacive character that most FE display, and to their large anharmonicities (beyond quartic order). These differences, though, are not too severe specially when considering the simplicity of the model.

We now consider the effects of compositional disorder. Following Ref. [26], we parametrize the quenched random electric fields by a Gaussian probability distribution with zero mean and variance \(\Delta^2\) (see supplement). Figures 3(a)-(b) show an schematic of the electric field-temperature \((E-T)\) phase diagram and the entropy function for moderate disorder. There are metastable paraelectric states with a stability region that extends to zero temperature. Ferroelectric states appear as local minima in the free energy at high temperatures and become stable below a coexistence temperature \(T_c < T^0\). The coexistence line of the polar and non-polar phases ends at a critical point \((T_{cr}, E_{cr})\). Weak first-order phase transitions are induced for electric fields greater than a threshold field \(E_{th}\) as they cross the region of stability of the metastable paraelectric phase. For fields smaller than \(E_{th}\), no macroscopic ferroelectric transition occurs with a spontaneous polarization. In typical relaxors such as PMN, \(E_{th} \approx 2\) kV/cm and \((T_{cr}, E_{cr}) \approx (240\) K, \(4\) kV/cm).\(^3\)

Figures 4(a)-(d) show the electric field and temperature dependences of the ECE for zero and moderate disorder. In both cases the peaks in \(\Delta S\) and \(\Delta T\) occur at their corresponding transition temperatures and increase monotonically with increasing applied field, as expected. For moderate disorder, however, \(\Delta S\) increases provided the applied field is greater than \(E_{th}\). This increment occurs because of the shortening of the correlation length, as indicated by Eq. (3). Though \(\Delta T\) is also affected by the shortening of the correlation length, it decreases with disorder as \(T_c\) shifts to lower temperatures.

![Fig. 5. (a)-(b) Calculated dependence of the ECE with compositional disorder for strong changes in the electric field \(\Delta E_0/E_{cr} = 0 \rightarrow 1.5\). (c)-(d) Calculated ECE of a FE with moderate compositional disorder \((\Delta^2/v_0)/(k_B T^0) = 2.0 \times 10^{-2})\) for several electric field strengths.](image)

Figures 5(a)-(b) show \(\Delta S\) and \(\Delta T\) for several disorder strengths and for a fixed change in the electric field \((\Delta E_0 > 0 \rightarrow E_{cr})\). The increment in \(\Delta S\) from weak-to-moderate disorder is clearly shown here together with the monotonic decrease in \(\Delta T\). For strong disorder, the ECE is weak since the dipoles are pinned by the random fields, therefore the entropy does not change significantly upon the application or removal of electric fields. Our model is qualitative and fairly good quantitative agreement with the ECE effect observed in typical relaxors where direct temperature measurements in PMN-PT show that a sharp peak in \(\Delta T\) shifts to higher temperatures and increases its magnitude with increasing PT concentration (up to the morphotropic phase boundary).\(^2\)

Figures 5(c)-(d) show \(\Delta S\) and \(\Delta T\) for several electric field strengths and for fixed (moderate) disorder. As the electric field changes increase, a broad peak develops in addition to the usual sharp one at \(T_c\). Such broad peak in \(\Delta T\) is commonly observed in relaxors and it is usually attributed to nanoscaled polar domains.\(^2\) However, our model predicts a broad peak occurs in \(\Delta T\) already in the absence of compositional disorder (where there are no polar nanodomains) for very strong fields. Therefore, the broad peak is simply the expected maximum in the ECE for a ferroelectric that is deep
in the supercritical regime, i.e., away from the critical point \((T, E_0) \gg (T_{cr}, E_{cr})\). We obtain similar results from GL theory (see supplement). Experimentally, this broad peak is not observed in conventional ferroelectrics as their breakdown fields are close to their critical fields, e.g., \(E_{br} \approx 10 \text{ kV/cm}^{33}\) and \(E_{breakdown} \approx 14 \text{ kV/cm}^{29}\) for BaTiO\(_3\).

Starting from well-known microscopic models of ferroelectricity, we have derived a meaningful figure of merit for the ECE in a wide class of FE materials. When defining a figure of merit for a caloric effect, we find crucial to account for the well-known non-linearities that occur near the FE transition. The large correlation lengths of fluctuations of polarization of FEs, result in a small ECE. We predict that ultraweak FEs such as those of the TSCC-family should exhibit figures of merit of about an order of magnitude larger than those of conventional displacive and disorder FEs. Shortening the correlation lengths should provide guidance for characterizing known caloric materials and designing new ones with enhanced performance.

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I. MICROSCOPIC MODEL

In this section we present the microscopic model from which we calculate the ECE. The model was recently proposed in Ref. [1] for relaxor ferroelectrics. We present it here for the sake of completeness. We focus on the relevant transverse optic mode configuration coordinate $u_i$ of the ions in the unit cell $i$ along the polar axis (chosen to be the $z$-axis). $u_i$ experiences a local random field $h_i$ with probability $P(h_1, h_2, ...)$ due to the compositional disorder introduced by the different ionic radii and different valencies of, say, Mg$^{2+}$, Nb$^{5+}$, and Ti$^{4+}$ in the typical relaxor (PMN)$_{1-x}$(PT)$_x$. The model Hamiltonian is

$$H = \sum_i \left[ \frac{\Pi_i^2}{2M} + V(u_i) \right] - \frac{1}{2} \sum_{i,j} v_{ij} u_i u_j - \sum_i h_i u_i - E_0 \sum_i u_i \tag{1}$$

where $\Pi_i$ is the momentum conjugate to $u_i$, $M$ is an effective mass, and $E_0$ is a static applied electric field. We assume the $h_i$’s are independent random variables with Gaussian probability distribution with zero mean and variance $\Delta^2$. $V(u_i) = \frac{\kappa}{2} u_i^2 + \frac{\gamma}{4} u_i^4$ is an harmonic potential with $\kappa, \gamma$ positive constants. $v_{ij}/e^* = \left\{ \begin{array}{ll} \frac{3(z_i - z_j)^2}{|R_i - R_j|^3}, & R_i \neq R_j, \\ 0, & R_i = R_j, \end{array} \right.$ is the dipole interaction where $e^*$ is the effective charge and $Z_i$ is the $z$-component of $R_i$. For future use, we denote $v_q = \sum_{i,j} v_{ij} e^{iq(R_i - R_j)}$ the Fourier transform of the dipole interaction, $v_0 = (4\pi z^2/3)$ the $q \to 0$ component of $v_q$ in the direction transverse to the polar axis $\hat{z}$ ($v_q$ is non-analytic for $q \to 0$), $n$ the number of unit cells per unit volume, and $a$ the lattice constant.

II. VARIATIONAL SOLUTION AND ENTROPY FUNCTION

In the present section, we briefly describe the variational solution of the problem posed by the Hamiltonian (1) and obtain an expression for the entropy function.

We consider a trial probability distribution, $\rho^{tr} = e^{-\beta H^{tr}}/Z^{tr}$ where $H^{tr} = \sum_i \frac{\Pi_i^2}{2M} + \frac{1}{2} \sum_{i,j} (u_i - p)G_{i,j}(u_j - p) - \sum_i h_i u_i$, is the Hamiltonian of coupled displaced harmonic oscillators in a quenched random field, and $Z^{tr} = \text{Tr} e^{-\beta H^{tr}}$ its normalization. Where $\Pi_i$ is the conjugate momentum of the displacement coordinate $u_i$ at site $i$ and $M$ is an effective mass.

We consider random fields $\{h_1, h_2, ...\}$ with Gaussian probability distribution $P(h_1, h_2, ...) = \frac{1}{\sqrt{2\pi\Delta^2}} e^{-h^2/(2\Delta^2)}$, $\rho^{tr}$ and $\Omega_q$ the frequency of the transverse optic mode at wavevector $q$ and it is given by the Fourier transform $\Omega_q = \frac{\gamma}{2M} \sum_i G_{i,j} e^{iq(R_i - R_j)}$. We define $G_{i,j}^{-1} = \left(1/\Omega_q^2 \right) \{ e^{-\beta q(R_i - R_j)} \}$.

The entropy $S$ is given as follows.

$$S = \frac{1}{N} \int_{-\infty}^{\infty} dh_1 dh_2 ... P(h_1, h_2, ...) \text{Tr} \rho^{tr} \ln \rho^{tr} \tag{2}$$

$$S = \frac{k_B}{N} \sum_q \left[ \frac{\beta \Omega_q^2}{2} \coth \left( \frac{\beta \Omega_q^2}{2} \right) - \ln \left( 2 \sinh \left( \frac{\beta \Omega_q^2}{2} \right) \right) \right].$$

$S$ depends on temperature $T = (k_B\beta)^{-1}$, the applied static field $E_0$, and the strength of compositional disorder $\Delta$. The adiabatic changes in temperature $\Delta T$ and isothermal changes in entropy $\Delta S$ presented in the main text are calculated from Eq. (2). The correlation length of the fluctuations of polarization, $\xi$, is given by the frequency of the transverse optic phonon at the zone center, $\xi/\alpha = (4\pi^3/3)(\xi/(\Omega_0^2))^{1/2}$.

III. BROAD PEAK IN THE ECE OF CONVENTIONAL FERROELECTRICS

In this section, we show that Ginzburg-Landau-(GL) theory predicts a broad peak in the ECE of conventional ferroelectrics. We consider the simple GL theory of Ref. [2] for the conventional ferroelectric BaTiO$_3$ (BTO) in an applied field $E_0$ along the (001) axis. Near the paraelectric-to-ferroelectric transition of BTO, the GL free energy is given as follows.

$$F = \frac{a(T - T_0)}{2} P^2 + \frac{b}{4} P^4 + \frac{c}{6} P^6 + \frac{d}{8} P^8 - PE \tag{3}$$
where $P$ is the polarization and $T_0 \simeq 400$ K is the supercooling temperature. The coefficients $a = 1.696 \times 10^6 \text{Nm}^2\text{C}^{-2}$, $b = 3.422 \times 10^9 \text{Nm}^6\text{C}^{-4}$, $c = 1.797 \times 10^{11} \text{Nm}^{10}\text{C}^{-6}$, $d = 3.214 \times 10^{12} \text{Nm}^{14}\text{C}^{-8}$ are determined from the dielectric susceptibility and heat capacity experiments.\(^2\) The isothermal changes in temperature $\Delta T = T_2 - T_1$, are calculated self-consistently from the relation $T_2 = T_1 \exp \left[(a/2C) \left(P^2(E_2, T_2) - P^2(E_1, T_1)\right)\right]$, where the temperature and electric field dependence of $P$ are determined by the standard minimization procedure of the free energy (3). $C$ is the contribution from the lattice to the specific heat.

In the electric field-temperature phase diagram of BTO the spinodal line begins at about $(E_0, T_0) \simeq (0, 405 \text{K})$ and ends at a critical point $(E_{cr}, T_{cr}) \simeq (10 \text{kV/cm}, 415 \text{K})$.\(^2\) The paraelectric-to-ferroelectric transition is discontinous along the spinodal line and it is continous at $(E_{cr}, T_{cr})$. BTO is supercritical above the critical point and no transition occurs.

Figure 1 (a) shows the adiabatic changes in temperature $\Delta T$ for BTO for several changes in the field strength, $\Delta E_0$. $\Delta T$ exhibits a single peak at the transition point for $(\Delta E_0 \lesssim 0 \rightarrow 100 E_{cr})$, as expected. For larger $\Delta E_0$’s than this, a broad peak develops. Clearly, this peak cannot be observed experimentally as the required fields are well beyond BTO’s breakdown electric field ($\simeq 14 \text{kV/cm}$).\(^3\)

![Graph showing adiabatic changes in temperature](image)

**FIG. 1.** Adiabatic changes in temperature, $\Delta T$ in the conventional ferroelectric BTO for several changes in the electric field strength $\Delta E_0$ applied along the (001) direction. A secondary, broad peak arises in $\Delta T$ in addition to that at the transition temperature for very large $\Delta E_0$.

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