



## Why is the electrocaloric effect so small in ferroelectrics?

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## 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 for a wide class of ferroelectric materials. Such figures of merit provide insight into the relation between the strength of the effect and the characteristic interactions of ferroelectrics such as dipolar 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. In addition, we bring into question other widely used but empirical figures of merit and facilitate understanding of the recently observed secondary broad peak in the electrocalorics of relaxor ferroelectrics. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4950788>]

The thermal changes that occur in ferroelectric (FE) materials upon the application or removal of electric fields are known as the electrocaloric effect (ECE).<sup>1–7</sup> The effect was first studied in Rochelle salt in 1930<sup>8</sup> and it is 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,<sup>9</sup> replace the widely used but inefficient small thermoelectric cooling devices such as Peltier coolers,<sup>2</sup> and lead to energy harvesting applications.<sup>4</sup> Moreover, developing cooling prototypes based on the ECE<sup>10–12</sup> 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  $\text{J K}^{-1} \text{mol}^{-1}$ .<sup>2</sup> FE thin films exhibit ECEs of about an order of magnitude larger than their bulk counterparts as they can withstand larger breakdown electric fields.<sup>13</sup> 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.<sup>14</sup>

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.<sup>2</sup> Here, we provide such insight by deriving meaningful figures of merit from well-known microscopic models of ferroelectricity. Our figure of merit allows 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 Landau theory<sup>15</sup> and those from heuristic arguments.<sup>16</sup> 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.<sup>16–28</sup> We find that the commonly observed secondary broad peak in the ECE of relaxors<sup>19,27</sup> 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.<sup>2,5</sup>

To illustrate the ideas presented above, we adhere to a simple microscopic model for displacive ferroelectrics with quenched random electric fields.<sup>29</sup> Such compositional disorder is typical of relaxor ferroelectrics such as the prototype  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN) and it arises from the different charge valencies and disordered location of the  $\text{Mg}^{2+}$  and  $\text{Nb}^{5+}$  ions. In the absence of disorder, it is a standard minimal model of ferroelectricity.<sup>15</sup> With disorder, the model gives a good starting point for the description of the static dielectric properties of relaxors.<sup>29,30</sup>

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.<sup>5</sup> 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.<sup>21</sup> Another difficulty is that Landau theory fails for relaxors. Landau theory is applicable away from the region of critical fluctuations of polarization that occur near the transition point. In conventional ferroelectrics, Landau theory works remarkably well since this region is narrow.<sup>15</sup> In relaxors, on the other hand, Landau theory is not expected to hold as the region of fluctuations is broad. We overcome both of these difficulties by calculating the ECE directly from the entropy function, as described in the supplementary material.<sup>31</sup>

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  $T_c^0$ . 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 (see supplementary material)<sup>31</sup>

$$\frac{|\Delta S(T, E_0)|}{Nk_B} = \frac{3\zeta a^2}{8\pi} [\xi^{-2}(T, E_0) - \xi^{-2}(T, 0)], \quad (1)$$

where  $\zeta$  is a dimensionless coefficient that depends on the lattice structure,  $a$  is the lattice constant, and  $N$  is the number of lattice sites.<sup>29</sup>  $\xi(T, E_0)$  is the correlation length of the exponentially decaying fluctuations of polarization at the field  $E_0$  and temperature  $T$ .<sup>15</sup> It is given by the (soft) frequency of the transverse optic phonon mode<sup>29</sup> and it diverges as  $\xi(0, T) \propto (|T - T_c^0|)^{-1/2}$  at the onset of the FE transition.<sup>15</sup> A similar relation is derived for the adiabatic changes in temperature

$\Delta T(T_1, E_0) = T_2 - T_1$  (see supplementary material)<sup>31</sup>

$$\frac{\Delta T(T_1, E_0)}{T_1} = \frac{3\zeta a^2}{8\pi} [\xi^{-2}(E_0, T_2) - \xi^{-2}(0, T_1)]. \quad (2)$$

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,  $(\xi(T, E_0)/a)^{-2} - (\xi(T, 0)/a)^{-2} \simeq (\zeta k_B n)^{-1} P_s^2(T, E_0)/C_{CW}$  in Eq. (1), which gives the standard results from Landau theory<sup>15</sup> and similar form to those derived from heuristic arguments.<sup>16</sup>  $P_s(T, E_0)$  is the polarization at temperature  $T$  and at field  $E_0$ ,  $C_{CW}$  is the Curie-Weiss constant, and  $n = N/V$  is the number of lattice points per unit volume  $V$ . At the phase transition,  $\Delta S(T_c^0, E_0)$  and  $\Delta T(T_c^0, E_0)$  of Eqs. (1) and (2) peak as the correlation length at zero field diverges ( $\xi(T_c^0, 0) = \infty$ ) 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.<sup>15</sup>

We now derive our figure of merit. By evaluating the correlation length at the critical temperature ( $\xi^{-2}(E_0, T_c^0) \propto (T_c^0/C_{CW})^{1/3}(E_0/P_s^0)^{2/3}$ ) in Eqs. (1) and (2), we obtain the magnitude of the ECE in terms of dielectric properties of a FE (see supplementary material)<sup>31</sup>

$$\frac{\Delta T(T_c^0)}{T_c^0} \simeq \frac{\Delta S(T_c^0)}{Nk_B} \propto \left(\frac{T_c^0}{C_{CW}}\right)^{1/3} \left(\frac{E_0}{P_s^0}\right)^{2/3}, \quad (3)$$

where  $P_s^0 = P_s(0, 0)$  is the saturated polarization at zero field. The coefficient of proportionality is a dimensionless number  $((1/2)(27/(4\pi))^{2/3} \simeq 0.8)$ . Eq. (3) is our figure of merit. A similar calculation for an order-disorder FE gives a figure of merit similar to that of Eq. (3) with two differences: the ratio  $T_c^0/C_{CW}$  is fixed to 1/3 (a well-known result of pure order-disorder models<sup>33</sup>) and a constant of proportionality of  $((1/3)^{1/3}(1/2)(27/(4\pi))^{2/3} \simeq 0.6)$ .

The available data confirm the non-linearity predicted by our simple model: Figure 1 shows that  $\Delta T \propto E_0^{2/3}$  near the ferroelectric transition of triglycine sulphate  $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$ . Similar scaling laws have been observed in the magnetocaloric effect.<sup>34</sup> 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.<sup>2,5</sup>

From Eq. (3) and data from the literature,<sup>35</sup> 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 FEs 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

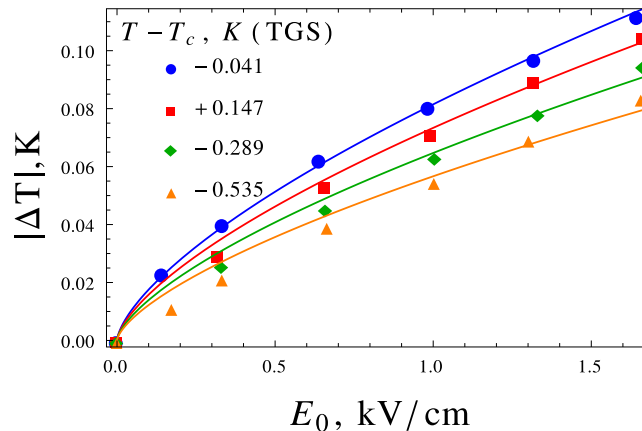


FIG. 1. Applied electric field dependence of the adiabatic changes in temperature near the paraelectric-to-ferroelectric transition ( $T_c^0 \simeq 322$  K) in triglycine sulphate (TGS). Solid lines correspond to fits to the electric field to the power of 2/3 as predicted by Eq. (3). Data taken from Ref. 32.

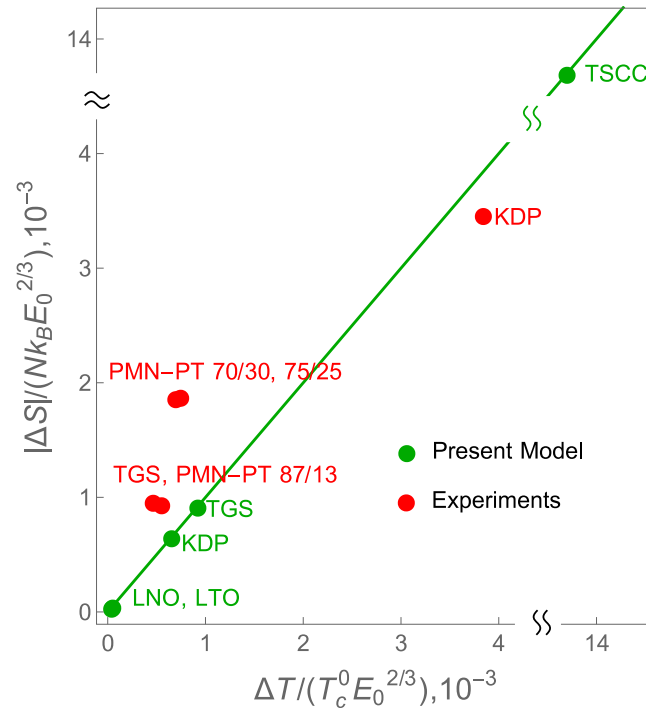


FIG. 2. Figures of merit at the paraelectric-to-ferroelectric transition for several ferroelectrics. Axes are in units of  $(\text{statvolt}/\text{cm})^{2/3}$ . Here, TSCC =  $(\text{CH}_3\text{NHCH}_2\text{COOH})_3\text{CaCl}_2$ , KDP =  $\text{KH}_2\text{PO}_4$ , TGS =  $(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4$ , LNO =  $\text{LiNbO}_3$ , LTO =  $\text{LiTaO}_3$ , and PMN-PT  $1-x/x = (\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3)_{1-x} - (\text{PbTiO}_3)_x$ . Data taken from Refs. 2, 32, and 36.

than those of displacive FEs). An exception to this rule may exist, however, in the ultraweak displacive FEs such as tris-sarcosine calcium chloride (TSCC). Our predicted figure of merit is an order of magnitude larger than any of the FEs considered here as a result of their exceptionally small Curie-Weiss constants and spontaneous polarization (which result in shorter correlation lengths).<sup>36</sup> The ECE has been recently measured in brominated TSCC compounds, however, we cannot compare to our model as the measurement was performed near its quantum critical point.<sup>37</sup> When Eq. (3) is contrasted to experiments,<sup>2</sup> there are clear discrepancies which we attribute to the mixed order-disorder and displacive character that most FEs 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. To do so, we consider the minimal model for relaxor ferroelectrics presented in Refs. 29 and 30. Such model includes dipolar interactions and short-range harmonic and anharmonic forces for the critical modes as in the theory of pure ferroelectrics together with quenched disorder coupled linearly to the critical modes. In formulating this model, it is important to recall Onsager's result<sup>38</sup> that unlike in the Clausius-Mossotti or Lorentz approximation, dipole interactions alone do not lead to ferroelectric order except at  $T = 0$ . Also that pure ferroelectric transitions were understood with the realization<sup>39</sup> that they are soft transverse optic mode transitions due to dipoles induced by structural transitions so that the low temperature phase does not have a center of symmetry. The first point is not, in practice, important for pure ferroelectrics which are well described by a mean-field theory for the dielectric constant, and is often a first order transition only below which the dipoles are produced.<sup>15</sup> But as it was shown in Refs. 29 and 30, in relaxors, the random location of defects acts in concert with the dipole interactions to extend the region of fluctuations to zero temperatures. Therefore dipole interactions must be a necessary part of the model. The essential physical points in the simplest necessary solution are to formulate a theory which considers thermal and quantum fluctuations at least at the level of the Onsager approximation<sup>38</sup> and random field fluctuations at least at the level of a replica theory. The model Hamiltonian and minimal solution are given in the supplementary material.<sup>31</sup>

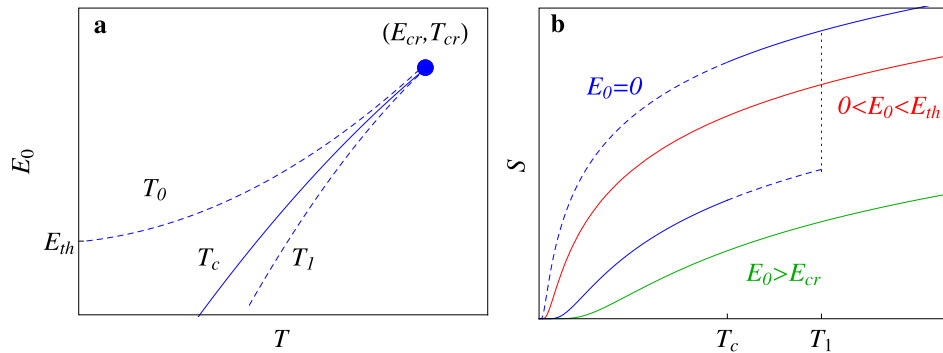


FIG. 3. (a) Schematic of the electric field-temperature phase diagram for ferroelectric with disorder. The coexistence line (blue) ends at a critical point  $(E_{cr}, T_{cr})$ . Spinodal curves  $T_0$  and  $T_1$  indicate the end of the stability of the paraelectric and ferroelectric states, respectively. (b) Schematic of the entropy-temperature phase diagram for various electric field regimes. Solid and dashed lines correspond to stable and metastable states, respectively. The entropy function for  $E_{th} < E_0 < E_{cr}$  is not shown for clarity.

Following Ref. 29, we parametrize the quenched random electric fields by a Gaussian probability distribution with zero mean and variance  $\Delta^2$ .<sup>31</sup> Figures 3(a) and 3(b) show the schematic of the electric field-temperature ( $E - T$ ) phase diagram and the entropy function for the 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  $T_c < T_c^0$ . The coexistence line of the polar and non-polar phases

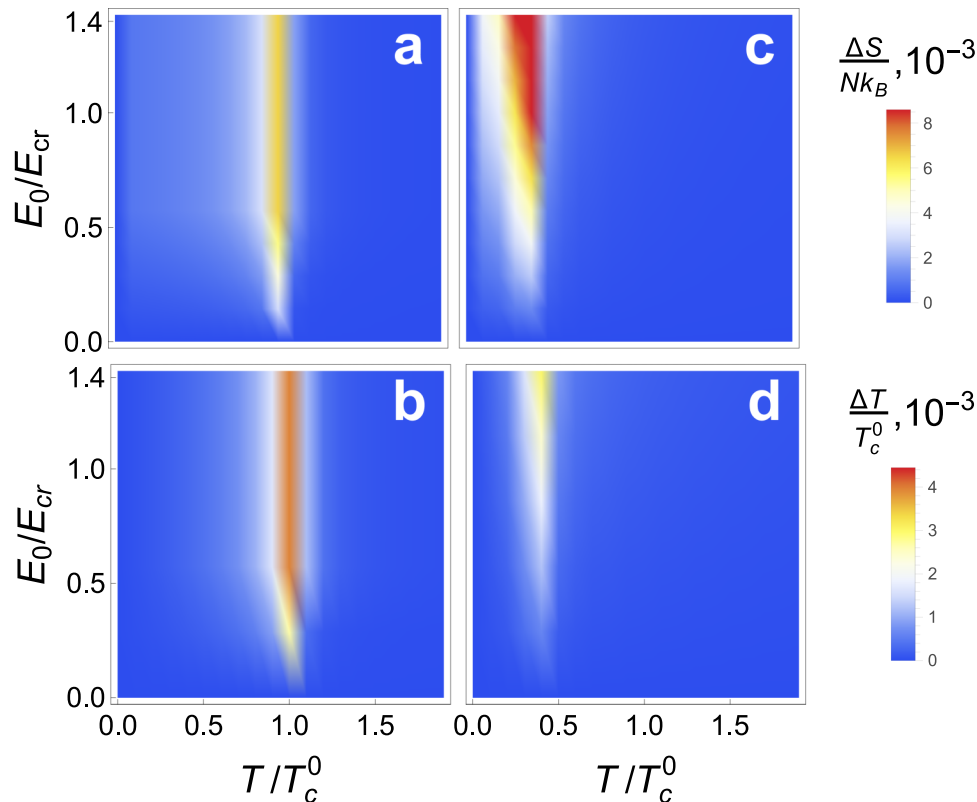


FIG. 4. Density plots of the adiabatic changes in temperature and isothermal changes in entropy for ((a) and (b)) no and ((c) and (d)) moderate ( $(\Delta^2/v_0)/(k_B T_c^0) = 2.0 \times 10^{-2}$ ) disorder. As expected,  $\Delta S$  and  $\Delta T$  in all cases are small except at the onset of the ferroelectric transition. For moderate disorder,  $\Delta S$  increases as a result the shortening of the correlation length, while  $\Delta T$  decreases as  $T_c$  shifts to lower temperatures.  $v_0$  is the zone-center Fourier component of the dipolar force.

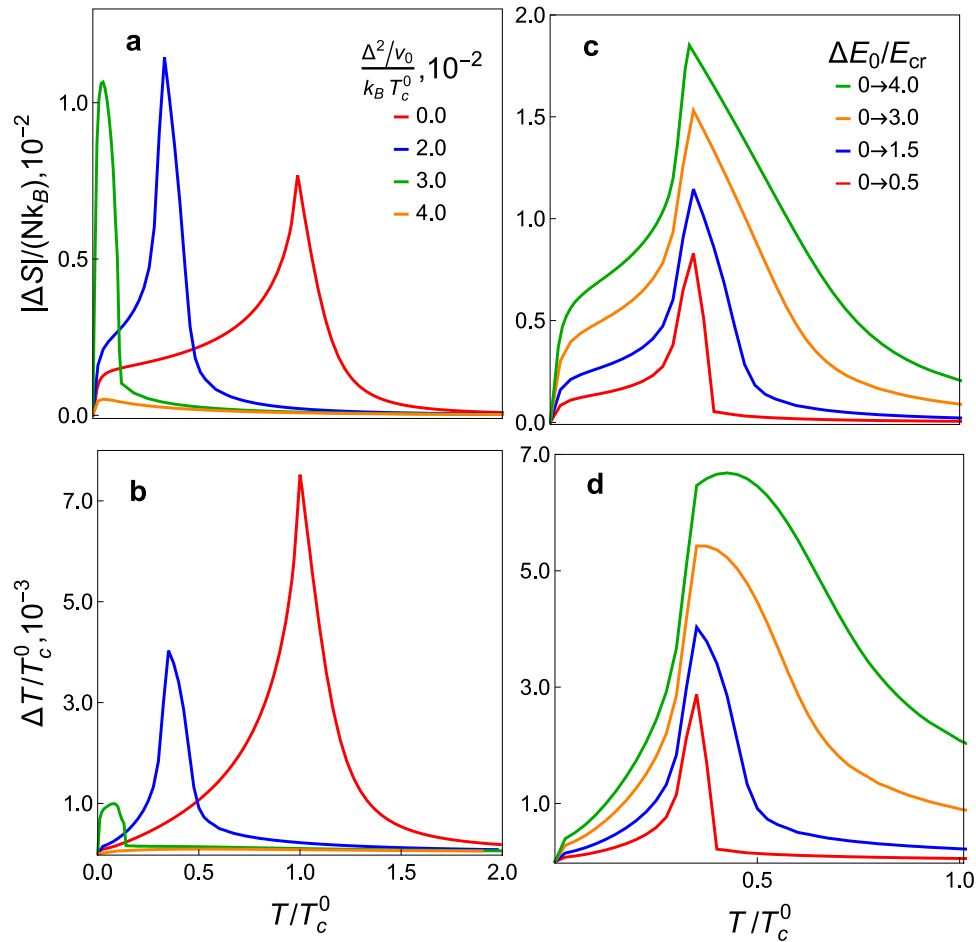


FIG. 5. ((a) and (b)) Calculated dependence of the ECE with compositional disorder for strong changes in the electric field  $\Delta E_0/E_{cr} = 0 \rightarrow 1.5$ . ((c) and (d)) Calculated ECE of a FE with moderate compositional disorder  $((\Delta^2/v_0)/(k_B T_c^0) = 2.0 \times 10^{-2})$  for several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

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).<sup>40</sup>

Figures 4(a)-4(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. We emphasize here that we are referring to the correlation length of fluctuations of polarization and not to the characteristic nanoscaled size of polar domains of relaxors.<sup>41</sup>

Figures 5(a) and 5(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).<sup>27</sup>

Figures 5(c) and 5(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.<sup>23,27</sup> 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 Landau theory.<sup>31</sup> Experimentally, this broad peak is not observed in conventional ferroelectrics as their breakdown fields are close to their critical fields, e.g.,  $E_{cr} \approx 10$  kV/cm<sup>42</sup> and  $E_{breakdown} \approx 14$  kV/cm<sup>35</sup> for BaTiO<sub>3</sub>.

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 order-disorder FEs. Shortening the correlation lengths results in larger isothermal changes in entropy, lower transition temperatures, and smaller adiabatic changes in temperature. Broad peaks in the ECE such as those that have been observed in relaxors are expected for any ferroelectric that can go well into the supercritical region. Our work has implications beyond the ECE as a similar analysis could be performed for other caloric effects such as magneto- and mechano-caloric effects, which are currently being studied extensively.<sup>2</sup> Our results in combination with other recently proposed figures of merit<sup>43,44</sup> should provide guidance for characterizing known caloric materials and designing new ones with enhanced performance.

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- <sup>1</sup> S. Crossley, N. D. Mathur, and X. Moya, *AIP Adv.* **5**, 067153 (2015).
- <sup>2</sup> X. Moya, S. Kar-Narayan, and N. D. Mathur, *Nat. Mater.* **13**, 439 (2014).
- <sup>3</sup> S. Pamir Alpay, J. Mantese, S. Trolier-McKinstry, Q. Zhang, and R. W. Whatmore, *MRS Bull.* **39**, 1099 (2014).
- <sup>4</sup> *Electrocaloric Materials: New Generation of Coolers*, edited by T. Correia and Q. Zhang (Springer-Verlag, Berlin, 2014).
- <sup>5</sup> M. Valant, *Prog. Mater. Sci.* **57**, 980 (2012).
- <sup>6</sup> J. Scott, *Annu. Rev. Mater. Res.* **41**, 229 (2011).
- <sup>7</sup> S. G. Lu and Q. M. Zhang, *Adv. Mater.* **21**, 1983 (2009).
- <sup>8</sup> P. Kobeko and I. Kurchatov, *Z. Phys.* **66**, 192 (1930).
- <sup>9</sup> S. Kar-Narayan and N. D. Mathur, *Ferroelectrics* **433**, 107 (2012).
- <sup>10</sup> S. Kar-Narayan and N. D. Mathur, *Appl. Phys. Lett.* **95**, 242903 (2009).
- <sup>11</sup> Y. Jia and Y. S. Ju, *Appl. Phys. Lett.* **100**, 242901 (2012).
- <sup>12</sup> H. Gu, X. Qian, X. Li, B. Craven, W. Zhu, A. Cheng, S. C. Yao, and Q. M. Zhang, *Appl. Phys. Lett.* **102**, 122904 (2013).
- <sup>13</sup> A. S. Mischenko, Q. Zhang, J. F. Scott, R. W. Whatmore, and N. D. Mathur, *Science* **311**, 1270 (2006).
- <sup>14</sup> B. Neese, B. Chu, S.-G. Lu, Y. Wang, E. Furman, and Q. M. Zhang, *Science* **321**, 821 (2008).
- <sup>15</sup> M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
- <sup>16</sup> R. Pirc, Z. Kutnjak, R. Blinc, and Q. M. Zhang, *J. Appl. Phys.* **98**, 021909 (2011).
- <sup>17</sup> L. Shebanov and K. Borman, *Ferroelectrics* **127**, 143 (1992).
- <sup>18</sup> A. S. Mischenko, Q. Zhang, R. W. Whatmore, J. F. Scott, and N. D. Mathur, *Appl. Phys. Lett.* **89**, 242912 (2006).
- <sup>19</sup> J. Hagberg, A. Uusimäki, and H. Jantunen, *Appl. Phys. Lett.* **92**, 132909 (2008).
- <sup>20</sup> T. M. Correia, J. S. Young, R. W. Whatmore, J. F. Scott, N. D. Mathur, and Q. Zhang, *Appl. Phys. Lett.* **95**, 182904 (2009).
- <sup>21</sup> S. G. Lu, B. Rožič, Q. M. Zhang, Z. Kutnjak, R. Pirc, M. Lin, X. Li, and L. Gorny, *Appl. Phys. Lett.* **97**, 202901 (2010).
- <sup>22</sup> M. Valant, L. J. Dunne, A.-K. Axelsson, N. McN. Alford, G. Manos, J. Peräntie, J. Hagberg, H. Jantunen, and A. Dabkowski, *Phys. Rev. B* **81**, 214110 (2010).
- <sup>23</sup> L. J. Dunne, M. Valant, A. K. Axelsson, G. Manos, and N. McN. Alford, *J. Phys. D: Appl. Phys.* **44**, 375404 (2011).
- <sup>24</sup> B. Rožič, B. Malič, H. Uršič, J. Holc, M. Kosec, and Z. Kutnjak, *Ferroelectrics* **421**, 103 (2011).
- <sup>25</sup> R. Pirc, Z. Kutnjak, R. Blinc, and Q. M. Zhang, *J. Appl. Phys.* **110**, 074113 (2011).
- <sup>26</sup> F. Le Goupil, A. Berenov, A. K. Axelsson, M. Valant, and N. McN. Alford, *J. Appl. Phys.* **111**, 124109 (2012).
- <sup>27</sup> J. Peräntie, H. N. Taylor, J. Hagberg, H. Jantunen, and Z.-G. Ye, *J. Appl. Phys.* **114**, 174105 (2013).
- <sup>28</sup> F. Le Goupil, A.-K. Axelsson, L. J. Dunne, M. Valant, G. Manos, T. Lukaszewicz, J. Dec, A. Berenov, and N. McN. Alford, *Adv. Energy Mater.* **4**, 1301688 (2014).
- <sup>29</sup> G. G. Guzmán-Verri, P. B. Littlewood, and C. M. Varma, *Phys. Rev. B* **88**, 134106 (2013).



- <sup>30</sup> G. G. Guzmán-Verri and C. M. Varma, *Phys. Rev. B* **91**, 144105 (2015).
- <sup>31</sup> See supplementary material at <http://dx.doi.org/10.1063/1.4950788> for model Hamiltonian, its approximate solution, and the calculation of the ECE from Landau theory for BTO.
- <sup>32</sup> B. A. Strukov, *Sov. Phys.-Crystallogr.* **11**, 757 (1967).
- <sup>33</sup> B. A. Strukov and A. P. Levanyuk, *Ferroelectric Phenomena in Crystals* (Springer, Berlin, 1998).
- <sup>34</sup> V. Franco and E. Conde, *Int. J. Refrig.* **33**, 465 (2010).
- <sup>35</sup> *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology—Ferroelectrics and Related Substances*, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1981), Vol. 16.
- <sup>36</sup> R. Mackeviciute, M. Ivanov, J. Banys, N. Novak, Z. Kutnjak, M. Wenka, and J. F. Scott, *J. Phys.: Condens. Matter* **25**, 212201 (2013).
- <sup>37</sup> S. E. Rowley, M. Hadjimichael, M. N. Ali, Y. C. Durmaz, J. C. Lashley, R. J. Cava, and J. F. Scott, *J. Phys.: Condens. Matter* **27**, 395901 (2015).
- <sup>38</sup> L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).
- <sup>39</sup> W. Cochran, *Phys. Rev. Lett.* **3**, 412 (1959); P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skanavi (Akad. Nauk SSSR Fizicheskii Inst., im P. N. Levedeva, Moscow, 1960).
- <sup>40</sup> Z. Kutnjak, R. Blinc, and Y. Ishibashi, *Phys. Rev. B* **76**, 104102 (2007).
- <sup>41</sup> Y. P. Shi and A. K. Soh, *Act. Mater.* **59**, 5574 (2011).
- <sup>42</sup> N. Novak, Z. Kutnjak, and R. Pirc, *EPL* **103**, 47001 (2013).
- <sup>43</sup> E. Defay, S. Crossley, S. Kar-Narayan, X. Moya, and N. D. Mathur, *Adv. Mater.* **25**, 3337 (2013).
- <sup>44</sup> X. Moya, E. Defay, V. Heine, and N. D. Mathur, *Nat. Phys.* **11**, 202 (2015).