Electrocaloric effects in multiferroics

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An atomistic effective Hamiltonian is used to compute electrocaloric (EC) effects in rare-earth substituted BiFeO 3 multiferroics. A phenomenological model is then developed to interpret these computations, with this model indicating that the EC coefficient is the sum of two terms, that involve electric quantities (polarization, dielectric response), the antiferromagnetic order parameter, and the coupling between polarization and antiferromagnetic order. The first one depends on the polarization and dielectric susceptibility, has the analytical form previously demonstrated for ferroelectrics, and is thus enhanced at the ferroelectric Curie temperature. The second one explicitly involves the dielectric response, the magnetic order parameter and a specific magneto-electric coupling, and generates a peak of the EC response at the Néel temperature. These atomistic results and phenomenological model may be put in use to optimize EC coefficients.

The electrocaloric (EC) effect is a phenomenon by which a material exhibits a reversible temperature change under the application/removal of an electric field [1–5]. It is attracting attention due to its potential to be an efficient solid-state refrigeration technology (see, e.g., Refs. [6–19] and references therein).

Furthermore, multiferroic effects that are driven simultaneously by more than one type of external physical handle, such as electric and/or magnetic fields, mechanical stress and pressure [20–24], are also promising to enhance change in temperature [23, 24].

Recently, multiferroics, which are materials that possess coupled long-range-ordered electric and magnetic degrees of freedom [25–31], have also been mentioned as possible systems to enhance the EC effects by taking advantage of such coupling [12, 20, 21, 32–34]. The pioneering work of Ref. [33] started from a phenomenological Landau-type equation for which coefficients were determined from first principles to investigate how magnetoelastic coupling modifies the EC coefficient. The main result was that EC effects are significantly enhanced (by about 60%) thanks to magnetoelastic coupling in the case that the ferroelectric and magnetic critical temperatures coincide. However, one has to be careful when using a Landau-type approach because fluctuations, which can be important for responses, are not treated explicitly and may be underestimated. That is why atomistic approaches incorporating couplings between electric dipoles and spins can be useful to also study EC effects in multiferroics, as the authors of Ref. [33] indicated. More importantly, it is presently unclear how to understand EC coefficients in multiferroics. For instance, can these coefficients be considered as composed of two terms, with one corresponding to that occurring in normal ferroelectrics and the second one related to the coupling between spins and electric dipoles? If yes, what are the precise quantities involved in the second term? Are they only magnetoelectric, or rather also involve electric and/or magnetic properties? Answering such questions will help in designing systems with large EC response.

The aim of this Letter is to resolve all these issues by (1) conducting atomistic-based simulations; (2) developing a simple model that can reproduce these simulations; and (3) using such simulations and model to gain a deep microscopic insight. We demonstrate that the EC coefficient of multiferroics can be thought as having two parts, each associated with different physical quantities.

Here, we adopt the effective Hamiltonian (H eff) approach developed in Ref. [35] to study disordered Bi 1−x Nd x FeO 3 (BNFO) alloys. H eff parameters are provided in the Supplemental Material (SM) [36]. This H eff successfully reproduced the temperature-versus-compositional phase diagram of BNFO. It predicts a R 3c ground state for small Nd compositions and a P m 3n phase for larger concentrations, with intermediate complex states in-between. Moreover, within the compositional range for which the R 3c phase is the ground state, the ferroelectric Curie temperature T C was numerically found to significantly decrease with the Nd composition while the T N Néel temperature is mostly independent of concentration, which also agrees with measurements [51–53]. The total internal energy of this H eff can be expressed as a sum of two main terms:

$$E_{tot} = E_{\text{BFO}}(\{u_i\}, \{\eta_i\}, \{\nu_i\}, \{\omega_i\}, \{m_i\})$$
$$+ E_{\text{alloy}}(\{u_i\}, \{\omega_i\}, \{m_i\}, \{\eta_{loc}\}),$$  

(1)

where $E_{\text{BFO}}$ is the H eff of pure BiFeO 3 [39–42] and $E_{\text{alloy}}$ characterizes the effect of substituting Bi by Nd ions. The H eff of BNFO contains four types of degrees of freedom: (i)
the local soft mode \{u_i\} centered on the A site of Bi or Nd ions in the 5-atom unit cell \(i\) (which is proportional to the local electric dipole moment of that cell \[43, 44\]); (ii) the strain ten-
sor gathering homogeneous \(\eta_H\) and inhomogeneous \(\eta_i\) contributions \[43, 44\]; (iii) the pseudovectors \{\(\omega_i\)\} that represent the oxygen octahedral tiltings \[45\]; and (iv) the magnetic moments \{\(m_i\)\} centered on Fe ions \[54\].

We employ this \(H_{\text{eff}}\) within Monte Carlo (MC) simulations on 12 \(\times\) 12 \(\times\) 12 supercells (containing 8 640 atoms) with per-
periodic boundary conditions and inside which Bi and Nd ions are randomly distributed over the A sublattice. 20 000 MC sweeps are used for equilibration and an additional 20 000 MC sweeps are employed to compute statistical averages at finite temperature, to obtain converged results. We also average our results over 10 random Bi/Nd distributions, to mimic well disordered BNFO solid solutions.

Regarding the linear electric coefficient, \(\alpha\), it is the derivative of the temperature with respect to electric field at constant en-
tropy. It can be obtained from MC simulations by taking ad-
vantage of the cumulant formula \[16, 17, 55\]:

\[
\alpha = \frac{-Z^* a_{\text{lat}} T}{\langle E_{\text{tot}}^2 \rangle - \langle E_{\text{tot}} \rangle^2 + \frac{2(\kappa_B T)^2}{N}} \left( \frac{\langle u_x E_{\text{tot}} \rangle - \langle u_x \rangle \langle E_{\text{tot}} \rangle}{\langle E_{\text{tot}}^2 \rangle - \langle E_{\text{tot}} \rangle^2 + \frac{2(\kappa_B T)^2}{N}} \right),
\]

where \(Z^*\) is the Born effective charge associated with the local
mode, \(a_{\text{lat}}\) represents the five-atom lattice constant, \(T\) is the temperature, \(u_x\) is the \(\gamma\)-component of the supercell average of the local mode with \(\gamma = x, y, z\) (note that the \(x, y, z\) axis are chosen along the pseudocubic \[100\], \[010\] and \[001\] directions, respectively), \(E_{\text{tot}}\) is the total internal energy given by the \(H_{\text{eff}}\), \(k_B\) is the Boltzmann constant, \(N\) is the number of sites in the supercell, and \(\langle \rangle\) defines the average over the MC sweeps at a given temperature \[56\]. In the following, we will denote \(\alpha\) the quantity defined by \(\frac{\alpha N^2}{\kappa_B T^2}\). Such defini-
tion corresponds to the EC response for an electric field applied along \[111\], which is the maximal response within a \(R3c\) state.

Figure 1 shows the EC coefficient as a function of tem-
perature for four different Nd compositions in disordered
\(\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3\). The results of Fig. 1 are obtained by start-
ing from 10 \(K\) adopting a \(R3c\) phase and then progressively heating up the BNFO solid solutions up to the con-
dition-dependent Curie temperature, \(T_C\) (for all investigated temperatures displayed in Fig. 1, the disordered \(\text{Bi}_{1-x}\text{Nd}_x\text{FeO}_3\) al-
loys possess the \(R3c\) phase from 0 \(K\) and up to \(T_C\)). This \(R3c\) state is characterized by a polarization lying along \[111\] and oxygen octahedra tilting in an antiphase fashion about this polar-
ization’s direction. These solid solutions also exhibit a G-type antiferromagnetic-to-paramagnetic transition at a Néel

\[
T_N, \text{ which is mostly independent on the com-
position and equal to \(\approx 660\) K} [35]. \text{ The SM} [36] \text{ provides some finite-temperature properties above } T_C.

Let us first focus on Fig. 1(a) that corresponds to a con-
centration of Nd equal to \(5\%\). The calculated \(T_C \approx 940\) K and \(T_N \approx 660\) K of \(\text{Bi}_{0.95}\text{Nd}_{0.05}\text{FeO}_3\) are in rather good agree-
ment with the measurements of \(T_C \approx 970\) K and \(T_N \approx 650\) K in \[52, 53\]. For any investigated temperature, \(\alpha\) basically mon-
tonically increases when the system is heated up to the Néel

temperature. It then adopts a small peak around \(T_N\), which is the maximal response within a \(R3c\) state.

\[
\frac{\alpha}{\kappa_B} = \frac{1}{2} \left( \frac{\kappa_B T}{C_{\text{ph}}} \right) \frac{d}{dT} \left( \frac{\kappa_B T}{C_{\text{ph}}} \right) \frac{\partial P_{\text{ph}}^2}{\partial T} \left| \frac{\partial P_{\text{ph}}}{\partial T} \right|, \text{ where } \frac{\partial P}{\partial T} = A_0 + A_1 T \text{ and } \frac{\partial P}{\partial T} = B_0 + B_1 T.
\]

\[
\frac{\partial P}{\partial T} = \frac{\partial P}{\partial T} \left( \frac{\kappa_B T}{C_{\text{ph}}} \right) \frac{\partial P}{\partial T} \left| \frac{\partial P}{\partial T} \right|, \text{ where } \frac{\partial P}{\partial T} = A_0 + A_1 T \text{ and } \frac{\partial P}{\partial T} = B_0 + B_1 T.
\]

\[
\frac{\alpha}{\kappa_B} = \frac{1}{2} \left( \frac{\kappa_B T}{C_{\text{ph}}} \right) \frac{d}{dT} \left( \frac{\kappa_B T}{C_{\text{ph}}} \right) \frac{\partial P_{\text{ph}}^2}{\partial T} \left| \frac{\partial P_{\text{ph}}}{\partial T} \right|, \text{ where } \frac{\partial P_{\text{ph}}}{\partial T} = A_0 + A_1 T \text{ and } \frac{\partial P_{\text{ph}}}{\partial T} = B_0 + B_1 T.
\]
more difficult to see its associated peak.

To understand the results in Fig. 1, we use a Landau free-energy potential $F(P, L, E, T)$ in which we substitute polarization $P$ and G-type antiferromagnetic (AFM) moment $L$ by their equilibrium values $P_s$ and $L_s$ found from minimization of free energy: $\frac{\partial F}{\partial P} |_{P=P_s, L=L_s, E, T} = 0$ and $\frac{\partial F}{\partial L} |_{P=P_s, L=L_s, E, T} = 0$. The minimized free energy $F_s(\mathcal{E}, T) = F(P_s, L_s, E, T)$ has the form:

$$F_s(\mathcal{E}, T) = \frac{1}{2} a(T) P_s^2(\mathcal{E}, T) + \frac{1}{4} b(T)L_s^2(\mathcal{E}, T) - \mathcal{E} P_s(\mathcal{E}, T) + \frac{1}{2} b(T) L_s^2(\mathcal{E}, T) + \frac{1}{4} \kappa L_s^4(\mathcal{E}, T) + \frac{1}{2} \epsilon L_s^2(E, T) P_s^2(E, T),$$

where $\mathcal{E}$ is the electric field.

Such equation implies that the polarization identity depends on magnetism, because of the $\frac{1}{4} c L_s^2(\mathcal{E}, T) P_s^2(\mathcal{E}, T)$ term. This equation is similar to the one used in Ref. [33]. The entropy described by this free energy $F_s(\mathcal{E}, T)$, composed of dipoles and spins, can then be obtained as

$$S_F(\mathcal{E}, T) = - \frac{dF_s}{dT} |_{\mathcal{E}} = \frac{a'(T)}{2} P_s^2(\mathcal{E}, T) - \frac{b'(T)}{2} L_s^2(\mathcal{E}, T),$$

where $a' = da/dT$ and $b' = db/dT$. Note that, here we took into account that $P_s$ and $L_s$ are found from minimization of the free energy.

In the case of a magnetic phase transition and presence of polarization, we can consider two parts of the total entropy $S(\mathcal{E}, T)$: A first one due to electric dipoles and spins (the active part treated by the Landau potential above, with entropy $S_F(\mathcal{E}, T)$) and a second one due to the rest of the lattice (the inert part that can be considered to be a trivial collection of harmonic phonons, with entropy $S_{ph}(T)$) [60, 61]. For an adiabatic process, we have:

$$\Delta S(\mathcal{E}, T) = \Delta S_F(\mathcal{E}, T) + \Delta S_{ph}(T) = 0. \quad (5)$$

Let $C_{ph}$ denote the heat capacity associated with the background lattice modes. Then the change of lattice entropy from an initial state $(0, T_0)$ to the final state $(\mathcal{E}, T)$ is given by:

$$\Delta S_{ph} = \int_{T_0}^{T} \frac{C_{ph}}{T} dT \equiv C_{ph} \ln \left( \frac{T}{T_0} \right). \quad (6)$$

Consequently, combining Eqs. (5) and (6) leads to

$$C_{ph} \ln \left( \frac{T}{T_0} \right) = - \Delta S_F = \frac{1}{2} a'(P_s^2 - P_0^2) + \frac{1}{2} b'(L_s^2 - L_0^2). \quad (7)$$

Here $P_s = P_s(\mathcal{E}, T), P_0 = P_s(0, T_0), L_s = L_s(\mathcal{E}, T), L_0 = L_s(0, T_0)$, where $T_0$ is the initial temperature and $T = T_0 + \Delta T$ is the final temperature (\(\Delta T\) represents the temperature change). Solving this equation with respect to $T/T_0$ yields:

$$(T_0 + \Delta T)/T_0 = e^{[a'(P_s^2 - P_0^2) + b'(L_s^2 - L_0^2)]/2C_{ph}}. \quad (8)$$

For small $\Delta T$:

$$\Delta T = \frac{T_0 \left[ a'(P_s^2 - P_0^2) + b'(L_s^2 - L_0^2) \right]}{2C_{ph}}. \quad (9)$$

One can then derive the following expression for $\alpha$ [10, 16]:

$$\alpha = \frac{\partial \Delta T}{\partial \mathcal{E}} \bigg|_S = \frac{T_0 a'(T) P_s}{2C_{ph}} \frac{\partial P_s^2}{\partial \mathcal{E}} \bigg|_T + \frac{T_0 b'(T) L_s^2}{2C_{ph}} \frac{\partial L_s^2}{\partial \mathcal{E}} \bigg|_T \varepsilon_0 \chi, \quad (10)$$

where $\varepsilon_0$ is the vacuum permittivity and $\chi$ is the dielectric susceptibility.

Finally, let us note that one could try to approximate $C_{ph}$ by adding a $k_B$ contribution for each degree of freedom belonging to the trivial – harmonic – part of the system. However, it is not obvious how to count the exact number of active and inactive variables in the framework of a Landau theory; we thus treat $C_{ph}$ as an adjustable parameter. Note that we did not fit $C_{ph}$ alone but rather the ratio of $a'(T)/C_{ph}$ and $b'(T)/C_{ph}$.

As shown by the green lines of Fig. 1, the second line of Eq. (11) fits well the MC data, when (1) using the $P_s$, $\chi$, $L_s$ and $\frac{\partial \delta}{\partial P}$ [62] obtained by our Monte-Carlo simulations (these four quantities are shown in Fig. 2 for the case of a 5% Nd composition); and (2) assuming that $C_{ph}$ and $b'(T)$ are fitting constants, while $a'(T) = A_0 + A_1 T$ with $A_0$ and $A_1$ are fitting parameters [63]. Since its validity is confirmed by Fig. 1, the second line of Eq. (11) can now be used to gain an insight [36] into the results of Fig. 1, via the decomposition of $\alpha$ into its two terms – that are $\frac{T_0 a'(T)}{C_{ph}} P_s \varepsilon_0 \chi$ and $\frac{T_0 b'(T)}{C_{ph}} L_s \frac{\partial L_s}{\partial \mathcal{E}} \bigg|_T \varepsilon_0 \chi$. The first contribution has precisely the analytical form of the EC coefficient for non-magnetic systems, see Refs. [16, 17]. It is shown by blue lines in Fig. 1, and is the one that contributes the most to the total $\alpha$ for any composition. Its increases with temperature and is driven by the corresponding increase in dielectric susceptibility, however moderated by the concomitant decrease in polarization [see Figs. 2(b) and 2(a)]. This first contribution implicitly depends on magnetism because of the coupling between polarization and antiferromagnetism, as evidenced in the change of behavior of the polarization and in the occurrence of a plateau in the dielectric response near $T_N$. 


(such behavior of $\chi$ has been reported in other multiferroics [39, 64]). The second contribution of Eq. (11) is depicted in brown lines in Fig. 1, and is basically independent on the investigated composition for any temperature. As evidenced in Fig. 1, it is the one responsible for the small peak of $\alpha$ found near the Néel temperature. This small peak becomes more difficult to be seen in the total EC coefficient (shown in green) when the Nd composition increases simply because the first contribution provides much larger values than the second contribution. Figures 2(c) and 2(d) also reveal that this small peak originates from the activation and then sharp increase of the magnitude of $\frac{\partial L}{\partial T}$ near $T_N$. This derivative for temperatures far away below $T_N$ is then basically a constant that characterizes intrinsic magnetoelectric coupling – which is related to the $c$ constant of Eq. (3). The second term of Eq. (11) tells us that the EC coefficient of a multiferroic can be optimized even at temperatures far away $T_N$ in systems possessing strong coupling between polarization and magnetic ordering. Ba(Sr,Ba)MnO$_3$ films may thus be a system of choice to investigate electrocaloric effects due to its strong magnetoelectric coupling [65–67].

The now-elucidated effect of $\frac{\partial L}{\partial T}$ on $\alpha$ near $T_N$ can be further used to address the finite-size effects in our computations of the EC coefficient. It is known that such size effect broadens the magnetic transition when decreasing the supercell size (see the SM [36]) [47, 48], and we also checked that the magnitude of the second contribution of $\alpha$ around $T_N$ increases when increasing such size. It will thus be more realistic, regarding what to expect in experiments, to rather adopt a $L_s = A|T_N - T|^\beta$ power law (see Refs. [47, 50]) near the Néel temperature, where $A$ and $\beta$ are coefficients. Consequently, we (1) chose to replace, around $T_N$, the MC data for $L_s$ by the result given by such power law with $\beta$ equal to 0.5 (mean-field value); (2) continue to still use the MC data for $L_s$ for temperatures far away (below) the Néel temperature; and (3) extract $A$ such by imposing that this power law of item (1) matches the MC data of item (2). Using the new resulting $\frac{\partial L}{\partial T}$ along with all the previous other quantities in Eq. (11) (including the temperature behavior of the polarization) provides the data given in Fig. 3 for the second contribution but also total EC coefficient in disordered Bi$_{0.95}$Nd$_{0.05}$FeO$_3$ alloys. The aforementioned change of $L_s$’s behavior, that is a more abrupt change near $T_N$, leads to a narrower and stronger peak of $\alpha$ close to the Néel temperature. The second contribution now amounts for 42% of the total EC coefficient near the magnetic transition. Such latter result is in-line with the phenomenological theory of Edström et al. [33] predicting that the magnetic contribution can reach approximately 60% of the electric contribution at the magnetic transition, and thus enhance the EC effect, in epitaxial multiferroic SrMnO$_3$ systems under a tensile strain of 2.63% – for which $T_N = T_C$. Our study explains why it is the case thanks to Eq. (11) that not only reproduces atomistic results but also and especially provides an insight into the microscopic origins of the EC effects in a multiferroic. We also used a larger supercell and such power law of $L_s$ with different $\beta$, and found that our qualitative results are still valid for any reasonable choice of $\beta$ (see Fig. S3 of the SM [36]). Note that the peak of Fig. 1(a) at the Néel temperature is significantly less pronounced than in Ref. [33] for two possible reasons. The first one is that such peak depends on the size of the simulation supercell (see the SM [36]) and the second one is that the magnetoelectric coupling is weaker in BiFeO$_3$ [39] than in SrMnO$_3$ [33]. Fluctuations within the $H_{eff}$ are also discussed in the SM [36].

In summary, an atomistic effective Hamiltonian scheme has been used to compute finite-temperature electrocaloric coefficients in the rare-earth substituted BiFeO$_3$ multiferroic. The results are then interpreted via the development of a model that reproduces these computational data. EC coefficients can be decomposed in two main terms. The first term takes into account the microscopic origins of the EC effects in a multiferroic. We also used a larger supercell and such power law of $L_s$ with different $\beta$, and found that our qualitative results are still valid for any reasonable choice of $\beta$ (see Fig. S3 of the SM [36]). Note that the peak of Fig. 1(a) at the Néel temperature is significantly less pronounced than in Ref. [33] for two possible reasons. The first one is that such peak depends on the size of the simulation supercell (see the SM [36]) and the second one is that the magnetoelectric coupling is weaker in BiFeO$_3$ [39] than in SrMnO$_3$ [33]. Fluctuations within the $H_{eff}$ are also discussed in the SM [36].

In summary, an atomistic effective Hamiltonian scheme has been used to compute finite-temperature electrocaloric coefficients in the rare-earth substituted BiFeO$_3$ multiferroic. The results are then interpreted via the development of a model that reproduces these computational data. EC coefficients can be decomposed in two main terms. The first term takes its largest value at the Curie temperature and explicitly depends on the polarization and dielectric susceptibility, that are both implicit functions of magnetic ordering and strength because

![FIG. 2. Temperature dependence of some properties in disordered Bi$_{0.95}$Nd$_{0.05}$FeO$_3$ alloys, as obtained from our MC simulations: (a) the macroscopic polarization $P_s$; (b) the average between the three diagonal elements of the dielectric susceptibility; (c) the AFM vector; and (d) the derivative $dL_s/dP_s$.](image-url)

![FIG. 3. Same as Fig. 1 (a) but now using a different $\frac{\partial L_s}{\partial T}$ (see text) in the second line of Eq. (11).](image-url)
of magnetoelectric couplings. The second term adopts a peak near the Néel temperature and is proportional to the antiferromagnetic vector, the polarization derivative of the antiferromagnetic vector and the dielectric susceptibility. Such findings therefore suggest an original way to induce large EC coefficients by simultaneous optimization of electric, magnetic and magnetoelectric properties at a selected temperature below the Néel temperature: (1) the dielectric susceptibility should be large; (2) the antiferromagnetic vector should be strong; and (3) the magnetoelectric coupling $\frac{d\alpha}{d\theta}$ should be large [68]. Our results and phenomenology should be valid for all magnetoelectric multiferroics, at the exception of those for which a magnetic Dzyaloshinskii-Moriya interaction involving the polarization (e.g., the spin-current model) is important. We hope that this present article deepens the fields of multiferroics and important subtle cross-coupling properties such as electrocaloric effects.

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Note that the denominator in this expression essentially corresponds to the calculated specific heat, which has several parts. The non-trivial one is associated from the potential energy of the subsystem described by our effective Hamiltonian (local dipoles, O$_6$ rotations, inhomogeneous strains and spins), and is given by the width of the energy distribution as obtained from our Monte Carlo simulations. The second, trivial part is associated to the kinetic contribution of all the lattice degrees of freedom in our material (15 per cell), as well as the contribution associated to the potential energy of the variables not included in our effective Hamiltonian (6 per cell); hence the term proportional to $2k_B T/2$. Note also that Eq. (2) is not suitable to describe situations in which the electric field induces a phase transition; hence, we restrict its application to relatively small electric fields.

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Note that the linear temperature dependence of $\alpha'(T)$ is needed for describing results far away from the Curie temperature, probably also because the oxygen octahedral tiltings are implicitly included in our model within some parameters of Eq. (11).

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