# A generalized thermodynamic theory of the multicaloric effect in single-phase solids

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## ARTICLE INFO

## ABSTRACT

The paper presents a generalized thermodynamic theory of the multicaloric effect ($\mu$CE) in single-phase solids. It is demonstrated that $\mu$CE consists of three well-known effects (electro-, magneto-, and elastocaloric) and three rather new ones that exist due to the interaction between the different fields. They are magnetoelectro-, piezoelectro-, and piezomagnetocaloric effects. Because of a coupling of six effects, it is difficult to identify a single effect in nonlinear materials. Therefore, the linear case is discussed first. Additionally, it is pointed out the necessity to take into account the influence of the gradients of thermodynamic variables on $\mu$CE. Such a focus has enabled us to predict the existence of a flexocaloric effect, that is a change of temperature or entropy with changing deformation gradient. The model is illustrated with data on BST, $BaTiO_3$, PZT ceramics, and $In_2NiMnO_6$ multiferroic.

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## 1. Introduction

In recent years, three caloric effects (CEs) – electro/ magneto/ elasto(baro)caloric – were widely reported and discussed (Alex Müller et al., 1998; Gschneidner et al., 2005; Kitanovski et al., 2015; Mischenko et al., 2006). These phenomena reflect the change of temperature and/or thermodynamic entropy of a system by the application or removal of an external field. The interaction between electrical, magnetic and elastic properties of the multiferroic material results in the appearance of multicaloric effect ($\mu$CE) and meaningful increase in CEs strength (Fähler et al., 2012; Kumar and Yadav, 2014; Lisenkov et al., 2013; Liu et al., 2014; Manosa et al., 2013; Meng et al., 2013; Moya et al., 2014; Planes et al., 2014; Starkov et al., 2011, 2012; Zvezdin et al., 2009). The most considerable effects are seen near the phase transition point of the materials used, where the internal parameters of the system are strongly temperature dependent.

In spite of a plethora of works devoted to the experimental and theoretical analysis, a historical overview of the phenomenon was omitted or drastically shortened. Although the term "multicaloric" is rather recent, it is possible to claim that the history of research on $\mu$CE has spanned over half a century. A pioneering work on the issue was conducted in parallel by Devonshire (1949) and Ginzburg (1949). These studies have not focused directly on the caloric effects, but investigated the relationship between the electric and elastic fields for barium titanate. Five years later, the impact of pressure on the tricritical points for ferromagnetic and ferroelectric materials was experimentally examined in the paper of Patrick (1954). Already in 1957, basic thermodynamic expressions describing CEs in the interaction of two fields, i.e. a particular case of the multicaloric effect, were reported for the first time in the book of Nye (1957). The equation (38) in Chapter 10 clearly determines the entropy change in the linear approximation for varying electric and elastic fields.

Unfortunately, after these first encouraging steps, the further progress in the area had slowed. In 1968, the influence of pressure on the electrocaloric effect (ECE) was studied by Zheludev (1968), who derived the equations for the various thermodynamic processes with constant stress and constant electric field. In-turn, the joint use of magnetic and elastic fields for the cooling purposes has been first proposed by Alex Müller et al. (1998) only in 1998. He analyzed both experimentally and analytically that caloric effects are strongest at the structural phase transition, and established the possibility to combine cooling methods in multiple ways. After five years, the thermodynamic theory for coupling of the elastic and magnetic fields was presented by Strässle et al. (2003). Flerov (2012) applied these findings to the model to describe the thermodynamic effects in the presence of three fields (electric, magnetic, elastic) simultaneously. However, the vector nature of the fields were not taken into account, and all the considerations were made using scalar variables and again in a linear approximation. A little later, the interaction between magnetic and ferroelectric

subsystems leading to caloric response was postulated on the ground of experiments by Zvezdin et al. (2009).

Finally, the term "multicaloric" appeared in 2010 in the experimental work of Mañosa et al. (2010). It was shown that the application of pressure to the magnetic shape-memory alloy gives rise to CE with a magnitude comparable to the giant magnetocaloric effect. As was theoretically predicted in Starkov et al. (2011, 2012), a significantly larger temperature change (3–5 times) with the caloric effect can be obtained by a consistent periodic application of the fields (parametric enhancement). In addition, in these papers, a thermodynamic description of the CEs coupling was originally derived in the framework of the Landau–Ginzburg model and introduced the new idea of the use of multiferroics in the solid-state coolers. Considerable interest in the multicaloric cooling appeared in 2012 after the publication of Fähler et al. (2012) paper, which describes the prospects and challenging tasks of the solid-state refrigeration. Unfortunately, the following article by Vopson (2012), released in the same year and dedicated to a similar topic, contains a number of errors (Starkov and Starkov, 2015), which have been repeated in a series of subsequent studies (e.g., in Flerov et al. (2015); Planes et al. (2014); Vopson (2013)). As an important outcome of the research on $\mu$CE, the conclusions on the strengthening of the cooling effect in the presence of several fields were confirmed by the first principles calculations by Lisenkov et al. (2013). Only recently, the measurements of the CEs coupling given in Flerov et al. (2015) conclusively show that $\mu$CE is not a simple sum of its constituent effects – electro- and elastocaloric (ElCE). It turned out, the interaction of electrical and elastic fields at certain temperatures leads to an approximate doubling of the multicaloric effect in comparison with the sum of ECE and ElCE.

At present, scrutinizing the impact of a single field, most of the models provide identical results. Although some questions of the theory of interaction between two CEs had been considered previously (Castán et al., 2012; De Oliveira, 2011; Manosa et al., 2013; de Medeiros et al., 2008; Meng et al., 2013), a successful attempt to move towards a complete thermodynamic theory of $\mu$CE, taking into account the gradients of thermodynamic quantities and their non-linear dependence in vector form, was made only in 2014 (Starkov and Starkov, 2014a). Another problem is the absence of an established terminology, even nowadays. For example, four CEs have been investigated in Fähler et al. (2012). The authors separately considered the barocaloric effect, which, as is demonstrated by Starkov and Starkov (2014c), is a part of the elastocaloric effect for either uniaxial or hydrostatic pressure. In Moya et al. (2014) ElCE is named mechanocaloric, and in Lisenkov et al. (2013) – piezocaloric. We believe that if there are three main fields: electric, magnetic, and elastic; then effects corresponding to these fields should be called by the names of the fields, i.e., electrocaloric, magnetocaloric and elastocaloric. However, the interplay of forces of different nature, quite obviously, can cause additional effects: magnetoelectrocaloric, piezoelectrocaloric, and piezomagnetocaloric. For instance, the toroidocaloric effect studied in Castán et al. (2012) was considered as an independent phenomenon. In our opinion, it should be understood as a particular case of the magnetoeletrocaloric effect. The listed above effects were reported in various ways and authors obtained different results at the final stage (cf. Planes et al. (2014); Starkov and Starkov (2014c)). Therefore, the main aim of this work is to accurately and comprehensively describe $\mu$CE and its corresponding components.

## 2. Thermodynamic theory of caloric effects

### 2.1. Gibbs free energy

To describe the thermodynamics of the system, we will use the internal energy $U$ and the Gibbs free energy $F$ given by (Castán

et al., 2012; Manosa et al., 2013; Planes et al., 2014; Starkov et al., 2012)

$$F = U - TS - x_i X_i. \tag{1}$$

Here $T$ is the temperature, $S$ is the entropy, $x_i$ are the generalized forces, and $X_i$ are the generalized coordinates ($i = 1, 2, \ldots, n$). In (1) the Einstein summation notation is used, i.e., repeated indices are summed over the Cartesian components. As the first step, we consider $U$ dependent only on the generalized forces and coordinates, but not on their derivatives. The general solution of the problem will be given in Section 4. Note that the initial internal energy depends on $\{x_i, S\}$, and after performing the Legendre transformation (transition from the internal to the free energy) $U$ in (1) depends on $\{X_i, T\}$. Thus, the extreme condition of the free energy $F$ leads to the relations (Castán et al., 2012; Planes et al., 2014)

$$X_i = \frac{\partial U}{\partial x_i}, \quad S = -\frac{\partial F}{\partial T}. \tag{2}$$

In turn, the entropy differential (Castán et al., 2012; Strässle et al., 2003)

$$dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial x_i} dx_i, \tag{3}$$

by taking into account the Maxwell relations and definition of the heat capacity $C$ in constant external fields (Nye, 1957), can be written in the form

$$dS = \frac{C}{T} dT + \frac{\partial X_i}{\partial T} dx_i. \tag{4}$$

This implies that the equations for the basic thermodynamic processes are (Castán et al., 2012; Nye, 1957)

$$dS_{\text{ist}} = \frac{\partial X_i}{\partial T} dx_i, \quad dT_{\text{ad}} = -\frac{T}{C} \frac{\partial X_i}{\partial T} dx_i. \tag{5}$$

The first relation in (5) describes the isothermal entropy change, while the second deals with the adiabatic temperature change.

Before turning to the details of the calculations, it is worth clarifying the notations and conventions that will be used in the paper. Henceforth, explicit expressions for temperature, which differ from the formulas for the entropy by the multiplier $T/C$, will not be written out. The indices $ist$ and $ad$ mean value of any quantity in an isothermal or adiabatic process. Also, the entropy and temperature increments corresponding to their differentials will be further denoted by $\Delta$.

### 2.2. Linear dependence between generalized forces and coordinates

First, we will examine a relatively simple example that allows us to obtain explicit analytical expressions for $\mu$CE. In most cases, it can be assumed that the internal energy is the quadratic form of the generalized coordinates $U = a_{ij} X_i X_j / 2$, where $a_{ij} = a_{ji}$ are some coefficients that may depend on temperature. Then, the relationship between the generalized forces and coordinates is given by the linear equations $x_i = a_{ij} X_j$ and

$$X_i = \chi_{ij} x_j. \tag{6}$$

The matrix of generalized susceptibilities $\chi$ is inverse of the matrix $a$. More complicated variant of the nonlinear relation between $x_i$ and $X_i$ (based on the Landau free energy) can be found in Planes et al. (2014); Starkov and Starkov (2014b).

For an arbitrary dependence of the internal energy on the generalized coordinates, the matrix $\chi$ should be understood as the Jacobian matrix of the transition from generalized forces to generalized coordinates $\chi_{ij} = \partial X_i / \partial x_j$. This way, the equation (5) becomes

$$dS_{\text{ist}} = \frac{\partial \chi_{ij}}{\partial T} x_i \, dx_j. \tag{7}$$