The induced magnetic and electric fields' paradox leading to multicaloric effects in multiferroics

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Magneto-electric effect in multiferroics implies that an applied magnetic field induces an electric polarization change in a multiferroic solid and vice versa, an applied electric field modifies its magnetization. The magneto-electric effect is a powerful feature of multiferroics and has attracted huge interest due to potential technological applications. One such possible application is the multicaloric effect in multiferroics. However, a closer examination of this effect and its derivation leads to a paradox, in which the predicted changes in one of the order phase at a constant applied field are due to the excitation by the same field. Here this apparent paradox is first explained in detailed and then solved. Understanding how electric and magnetic fields can be induced in multiferroic materials is an essential tool enabling their theoretical modelling as well as facilitating the introduction of future applications.

1. Introduction

Multiferroics are very interesting materials with multi-functional properties. Following the initial surge in interest in the field of magneto-electric multiferroics in 1950s and 1960s [1-4], the topic has lost somehow interest with the scientific community. Recently, the interest in magneto-electric multiferroics grew substantially [5] because of the realization of their potential for technological applications. Wood and Austin summarized many possible applications of multiferroics in an article published in 1973 [6]. A more recent comprehensive review article detailing possible modern applications of multiferroics was published by Vopson in 2015 [7]. One such recently proposed application of multiferroics is their utilization to ultra-efficient solid state refrigeration via a new effect, characteristic only to multiferroics, the multicaloric effect [8]. The recently discovered multicaloric effect [8] is a significant breakthrough because it combines the principles of electrocaloric, magnetocaloric and even elastocaloric effects into a unified process with enhanced caloric properties [9]. The multicaloric effect is defined as the adiabatic temperature change in multiferroics activated by a single excitation (electric, magnetic or elastic) and it is mathematically described by the general equation of the giant multicaloric effect:

$$\Delta T = -\frac{T}{C} \cdot \sum_{i; i \neq j} \int_{x_j} \left[\left(\frac{\partial X_i}{\partial T} \right)_{x_j} \cdot \frac{\alpha_{ij}}{\chi_i} + \left(\frac{\partial X_j}{\partial T} \right)_{x_i} \right] \cdot dx_j \tag{1}$$

where: X_i = Magnetization (M), Polarization (P), Volume (V), Strain (ε),… are the independent variables; x_i = magnetic field (H), electric field (E), mechanical stress (σ),… are the generalized forces / fields thermodynamically conjugated to the generalized variables / displacements X_i; χ_i is the generalized susceptibility in the linear approximation ($\partial X_i / \partial x_i$) = χ_i; α_{ij} is the generalized linear magneto-electric coupling coefficient $\alpha_{ij} = \alpha_{ji} = (\partial X_j / \partial x_i)_{T, x_j \neq i} = (\partial X_i / \partial x_j)_{T, x_i \neq j}$; T is the operation temperature and it is a constant; C is defined as the heat capacity of the system at the operation temperature, T, also assumed constant, but it is acknowledged that in reality this is a strong approximation as the heat capacity has some non-negligible variation

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with the applied fields. A full derivation of relation (1) is given in [9], showing that the cross couplings between displacements and fields / forces play an important role in the multicaloric effect. For a finite adiabatic change in the applied external field x_i, a variation in temperature ΔT is produced resulting in the enhancement of the total temperature change ΔT due to the cross coupling additional terms $\alpha_{ij}/\chi_i \cdot (\partial X_i / \partial T)$. If (1) is applied to the particular case of a multiferroic material containing electric and magnetic order phases, the electrically and magnetically induced multicaloric effects are described by:

$$\Delta T_E = -\frac{T}{C} \cdot \int_{E_i}^{E_f} \left[\frac{\alpha_e}{\mu_0 \chi^m} \cdot \left(\frac{\partial M}{\partial T} \right)_{H,E} + \left(\frac{\partial P}{\partial T} \right)_{H,E} \right] \cdot dE \tag{2}$$

$$\Delta T_H = -\frac{T}{C} \cdot \int_{H_i}^{H_f} \left[\left(\frac{\partial M}{\partial T} \right)_{H,E} + \frac{\alpha_m}{\varepsilon_0 \chi^e} \cdot \left(\frac{\partial P}{\partial T} \right)_{H,E} \right] \cdot dH \tag{3}$$

However, the derivation of relations (1)-(3) in ref. [8, 9] appears to contain an apparent paradox, which would invalidate the proposed multicaloric effect. This apparent paradox and its solution will be discussed in the next sections. The discussion is limited to the particular case of a multiferroic material containing electric and magnetic order phases, for which multicaloric effects are described by (2) and (3).

2. The paradox

Applying an external E field to a dielectric polar material has the effect of changing its electric polarization. If the material is a multiferroic, the effect of the E field application is to modify its electric polarization and magnetization, according to the magneto-electric coupling effect. The converse magneto-electric effect is also valid, when a magnetic field applied to a multiferroic results in changes of not only magnetization of the material, but also its electric polarization.

The magneto-electric effect is an undisputed fact, proven experimentally in single phase [10] and composite multiferroics [11-13].

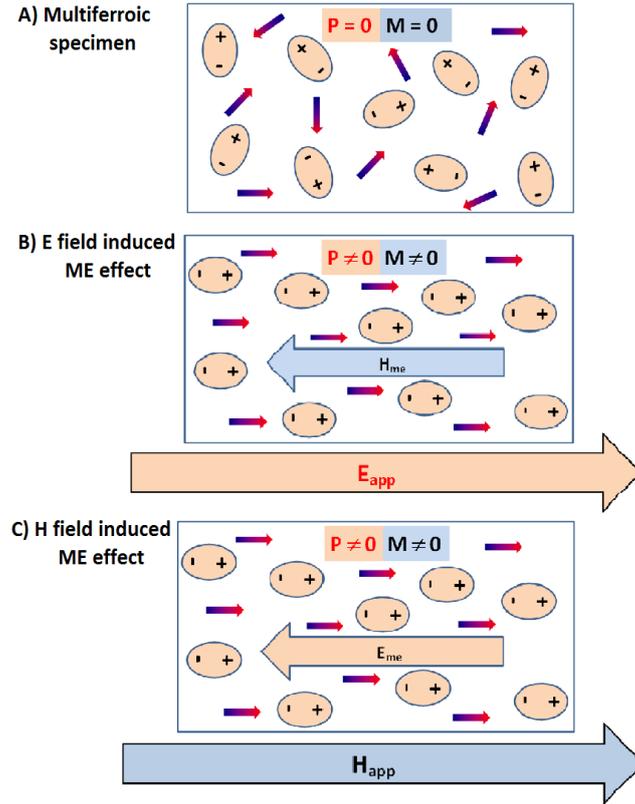However, the physical explanation of the effect is not so developed. There are indeed

Figure 1. Schematic representation of the magneto-electric (ME) effect in multiferroics. A) Multiferroic specimen with ovals indicating electric dipole moments and arrows indicating magnetic moments. B) Electrically activated ME effect showing the spontaneous occurrence of the ME induced H_{me} field. C) Magnetically activated ME effect showing the occurrence of the ME induced E_{me} field.

a number of microscopic models attempting to explain the magneto-electric coupling, but they have usually very limited applicability in terms of crystal symmetries, or the nature of ferroelectric phase in the multiferroic. Thermodynamically, the magneto-electric coupling coefficient results immediately from Maxwell equations applied to the differential Gibbs free energy of a multiferroic system, without any reference to possible microscopic mechanisms responsible for the coupling [7]. One way of approaching this problem is to regard the magneto-electric effect as the result of fictitious fields induced spontaneously in the material. That is equivalent to saying that the magnetization changes in a multiferroic in response to an applied electric field are due to a spontaneously induced magnetic field inside the material. The converse effect also produces a spontaneous electric field inside the material as a result of the application of a magnetic field. These cases are graphically represented in Figure 1. A) and B). The introduction of the fictitious field is critical for the derivation of relations (2) and (3).

Let us now examine this approach for the electrically induced magneto-electric effect, which is mathematically expressed in integral form as:

$$dM = \alpha_e dE \tag{4}$$

where α_e is the electrically induced magneto-electric effect. However, magnetization can be expressed in terms of linear change with a magnetic applied field as:

$$dM = \mu_0 \chi^m dH \tag{5}$$

From the two relations, one could easily deduce the induced magnetic field by an electric applied field in a multiferroic as:

$$dH = \frac{\alpha_e}{\mu_0 \chi^m} dE \tag{6}$$

Relation (6) and its electrical equivalent have been used in [8] to derive the multicaloric effect equations (1) and (2). However, at a closer inspection it appears that relation (6) is incorrect. Let us write the differential expression of the magnetization, talking in account the independent variables and constants:

$$dM = \left(\frac{\partial M}{\partial T}\right)_{H,E} dT + \left(\frac{\partial M}{\partial E}\right)_{H,T} dE + \left(\frac{\partial M}{\partial H}\right)_{T,E} dH \tag{7}$$

From (7), the correct expression of relation (4) is written by talking in account that the change in magnetization occurs at constant H and T is:

$$dM_{T,H} = \alpha_e dE \tag{8}$$

where α_e is the electrically induced ME coupling coefficient. From (7), we can also extract the change in magnetization that occurs at constant T and E, which is the equivalent of expression (5):

$$dM_{T,E} = \mu_0 \chi^m dH \tag{9}$$

If we now recombine (8) and (9) to obtain relation (6), we get:

$$dM_{T,E} = dM_{T,H} = \alpha_e dE \tag{10}$$

Relation (10) leads to a paradox, in which the change in magnetization obtained under constant electric field is related to the change in the electric field, $dM_{T,E} = \alpha_e dE$, which is clearly erroneous, as this would be zero. This fallacy would make relation (6) invalid, indicating that there can be no induced magnetic field by an electric field and vice versa in multiferroics. It would also invalidate the Multicaloric Effect equations (1) and (2) published in [8].

3. The solution to the paradox

In classical terms, at constant temperature, stress and other environmental conditions, magnetization can only be modified by the application of a magnetic field. Therefore, the change in magnetization *dM* in multiferroics due to the application of the electric field *dE* can be attributed to a <u>fictitious</u> magnetic applied field, induced by the magneto-electric effect dH_{me}. This field must not be confused with *dH* used in relation (7), as this field results from the magneto-electric coupling and it is induced internally by the application of the *E* field. Introducing the <u>fictitious</u> *H* field is very common in other well-established theories. For example, in the molecular field theory of ferromagnetism, Weiss treated ferromagnets as paramagnets by postulating the existence of an additional <u>fictitious</u> magnetic field whose origin is not given. Weiss [14] called this a *molecular field* [P. Weiss, *L'Hypothese du champ Moleculaire et de la Propriete Ferromagnetique*, J. de Phys. **6**, (1907) pp. 661-690]. Neel also used a similar approach when he introduced a <u>fictitious</u> fluctuating magnetic field in order to explain time dependent and relaxation phenomena in magnetic materials. Moreover, introducing a <u>fictitious</u> magnetic field in order to explain the magnetization change due to an applied electric field in multiferroics, is not a new idea. Rado et al. has introduced this idea in his 1961 papers [2,3], which were some of the very first studies of the magneto-electric coupling in Cr_2O_3. However, Agyei & Birman wrote one of the best papers detailing and categorizing various conditions of the occurrence of a spontaneous internal E or H field due to the changes in P or M as a result of the application of H or E, respectively [15].

With this in mind, let us re-write relation (7), by taking into account the applied magnetic field and the induced magnetic field due to the magneto-electric effect. This is achieved by replacing *dH* with:

$$dH = dH_{app} - dH_{me} \tag{11}$$

Relation (11) shows that the acting magnetic field on the multiferroic is a combination of the externally applied magnetic field, H_{app} and the induced magneto-electric field, H_{me}, where the minus sign indicates that the induced magneto-electric field is opposed to the applied field as dictated by Newton's 3rd law, or its extension to magnetic phenomena, Lenz's law. Using (11), relation (7) should then be written as:

$$dM = \left(\frac{\partial M}{\partial T}\right)_{H,E} dT + \left(\frac{\partial M}{\partial E}\right)_{H,T} dE + \left(\frac{\partial M}{\partial H}\right)_{T,E} dH_{app} - \left(\frac{\partial M}{\partial H}\right)_{T,E} dH_{me} \qquad (12)$$

Electrically induced magneto-electric effect implies that there is no external applied magnetic field, or the magnetic applied field is constant (i.e. change of M due to E applied only). Hence, $dH_{app} = 0$ and the third term in (12) vanishes. On the other hand, the induced field dH_{me} is the proposed fictitious field that occurs spontaneously due to the application of the E field (see figure 1. B). According to Lenz's law, the strength of the induced field dH_{me} is exactly as large as needed to account for the change in magnetization M via the well-known magneto-electric effect due to the application of E. This is also the meaning of the negative sign in (11). Therefore, at constant T and H (or zero applied magnetic field), the change dM should be zero as the effect of the applied E field on M is cancelled out by the occurrence of the induced field. Relation (12) is then:

$$dM_{T,H_{app=0}} = \left(\frac{\partial M}{\partial E}\right)_{H_{app=0},T} dE - \left(\frac{\partial M}{\partial H}\right)_{T,H_{app=0}} dH_{ME} = 0 \qquad (13)$$

Relation (13) leads to:

$$\left(\frac{\partial M}{\partial E}\right)_{H_{app=0},T} dE = \left(\frac{\partial M}{\partial H}\right)_{T,H_{app=0}} dH_{ME} \qquad (14)$$

or re-written as:

$$\alpha_e dE = \mu_0 \chi^m dH_{ME} \qquad (15)$$

Finally, from (15) we re-obtain relation (6) of the induced magnetic field due to the application of an electric field in a magneto-electric multiferroic:

$$dH_{ME} = dH = \frac{\alpha_e}{\mu_0 \chi^m} dE \qquad (16)$$

Relation (16) is identical to (6). The same formalism can be easily applied to the converse magneto-electric effect leading to induced internal electric field due to the application of a magnetic field:

$$dE_{ME} = dE = \frac{\alpha_m}{\varepsilon_0 \chi^e} dH \qquad (17)$$

It is important to mention that this is a simplified thermodynamic approach where the vector and tensor components have been neglected. For example the magneto-electric coupling coefficient is, strictly speaking, a second rank tensor with 9 components, α_{ij}. In most cases the crystal symmetry and/or experimental geometry reduces significantly the magneto-electric coupling tensor to one or a few dominant components, but the applicability of these relations must be strictly considered in

terms of E and H field vector components and their relationship to the sample geometry, crystal symmetry and directions of polarization and magnetization. This is particularly important when an antiferromagnetic phase exists in the multiferroic or when the sample geometry displays strong spatial variations.

4. Conclusions

Changes of electric polarization due to the application of a magnetic field, or magnetization due to the application of an electric field in a multiferroic material, are thermodynamically predicted to occur via the magneto-electric effect. This is well established and there is strong experimental evidence of this effect in both single-phase and composite multiferroics. The magneto-electric coupling mechanism in strain-mediated composite multiferroics is very well understood. However, despite numerous theoretical and experimental studies, the physical mechanisms responsible for the magneto-electric coupling effect in single-phase multiferroics are not fully understood. In this article it has been shown that a useful tool is to assume that these ferroic order changes are the result of fictitious induced electric and magnetic fields. This approach leads to useful relations linking the excitation field to the induced field in multiferroics, which in turn can be used to predict new effects such as the multicaloric effect, or to theoretically model the properties of multiferroics. The apparent contradiction of these induced fields is also discussed in detail and solved within a thermodynamic framework.

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