Temperature hysteresis in bilayer FeRh/PZT structure

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Abstract. We investigate temperature hysteresis of magnetization in a two-layer composite structure composed of magnetocaloric and electrocaloric materials. The proposed model describes the simultaneous application of electric and magnetic fields. Such an approach allows analysing features of multicaloric effect in bilayer FeRh/PZT structure. To verify the correctness of the developed model, the theoretical results are compared with the experimental data for the multicaloric effect in the FeRh-PZT structure.

1. Introduction

In recent years, multiferroics are considered as perspective materials for solid-state coolers, due to the coexisting of magnetocaloric, electrocaloric and elastocaloric effects. Multiferroics with two or more calorific effects are called multicalories and observing in them calorific effect is named multicaloric effect (µCE) [1, 2]. With a direct µCE, a change in entropy or temperature occurs with a simultaneous change in the electric, magnetic or elastic field. When the temperature changes, the crystal lattice deforms, which leads to the appearance of an electric and magnetic field, as well as to the appearance of elastic stresses. This effect is called the inverse µCE. For natural materials, these effects are very small. An increase in µCE is possible in multiferroics with strong pairwise interaction of the fields. The electric and elastic fields (the piezoelectric effect) interact most strongly, and the electric and magnetic fields interact most weakly (the magnetoelectric effect). Since the magnetoelectric susceptibility α characterizing the magnetoelectric effect is small, composite materials are used to increase it. Laminate composites are the simplest materials to produce, for which a substantial increase in α is possible. For example, the value of α is 1.6 · 10⁻⁵ sm⁻¹ for a two-layered structure of Fe₅₀ Rh₅₀ and BaTiO₃ layers [3]. This is five orders of magnitude more than in the best natural materials. Thus, of undoubted interest is the study of µCE in a bilayer composite composed of magnetocaloric and electrocaloric materials. Caloric effects are noticeable near phase transitions, where elasticity plays an important role, and all three of the above fields interact in such system. The main goal of this research is to study the temperature hysteresis of magnetization as a crucial feature of µCE within the Landau model. For the model demonstration and validation, we used a...
composite consisting of magnetic Fe_{48}Rh_{52} (FeRh) and piezoelectric PbZr_{0.53}Ti_{0.47}O_{3} (PZT) layers.

2. Magnetic, electric, and elastic fields in a thin bilayer plate

Let us consider a bilayer plate depicted in figure 1. The thickness of the piezoelectric layer is denoted by $h^{e}$ and the thickness of the magnetic layer by $h^{m}$. For the total thickness and the relative thicknesses we introduce the notations $h = h^{e} + h^{m}$ and $\vartheta^{e} = h^{e}/h$, $\vartheta^{m} = h^{m}/h$, respectively. The plate is assumed to be thin: its width of $A$ and the length of $B$ is much greater than $h$. Hereinafter, we designate by a subscript $e$ all the coefficients related to the piezoelectric layer and to the magnetic one by $m$. In turn, we employ the subscripts $e$ and $m$ for variables. In some cases, we omit these indices in order not to duplicate the same type of equality. To describe the structure properties in the Cartesian coordinate system $(x_{1}, x_{2}, x_{3}) \equiv (x, y, z)$, we use the electric and magnetic field strengths $E$ and $H$, polarization $P$ and magnetization $M$, displacement vector $u$, strain $u_{ij} = (u_{i,j} + u_{j,i})/2$ and stress $\sigma_{ij}$ tensors.

Note that the electric and magnetic fields directed across the layers along the $x_{3}$ axis (see, figure 1). Therefore, we may assume that the quantities $E, H, P, M$ are scalars. The electric field $E_{e}$ can be considered known and defined as $E_{e} = U/h^{e}$ for the electrodes connected only to the piezoelectric layer. Here $U$ is the applied potential difference. If the electrodes are connected to the edges of the plate, then the arising electric field is much less than this value. This decrease is explained by the fact that in a layered system the electric field is inversely proportional to the dielectric constant of the layer, and the dielectric constant of piezoelectrics as a rule is large.

The free energies of the layers $F^{e}$ and $F^{m}$ are written as [4]

$$F^{e} = \chi^{ee}P^{2} / 2 - PE + \chi^{me}M^{2} / 2 - MH + c_{ijkl}^{e}u_{ij}u_{kl} - e_{3jk}u_{jk}E, \tag{1}$$

$$F^{m} = \chi^{em}P^{2} / 2 - PE + aM^{2} / 2 + bM^{4} / 4 + cM^{6} / 6 - MH + c_{ijkl}^{m}u_{ij}u_{kl} - q_{ij33}u_{ij}M^{2}.$$

Here $\{a, b, c\}$ are the Landau coefficients, $\chi^{me}$ is the magnetic susceptibility of the piezoelectric layer, $\chi^{ee}$ and $\chi^{em}$ are the electric susceptibility of the piezoelectric and magnetic layers, $c_{ijkl}^{e}$ is...
the elastic moduli, $q_{j33}$ are the magnetostriction coefficients, $e_{3jk}$ are the piezoelectric constants.

In the last two sets of coefficients, subscript 3 indicates that polarization and magnetization have only one component, i.e. the third. When writing out the free energy (1), the Einstein convention was used: summation is performed over repeated indices. All coefficients are assumed to be independent of temperature $T$ except for the coefficient $a$ for which a linear dependence on temperature is assumed, $a = a_0(T - T_m)$. Here $T_m$ is the phase transition temperature for the magnetic layer and $a_0$ is some constant.

As the phase transition temperature for PZT lies substantially above room temperature, a linear relationship between the electric field and polarization is used to describe the piezoelectric layer. For the magnetic layer, the temperature $T_m$ is 315 K, i.e. close to the room temperature and the Landau model can be applied to describe this layer. Varying the free energies $F^e$ and $F^m$ leads to a system of equations

$$
\begin{cases}
P = \chi^{ee}E_e + e_{31}(u^{e}_{11} + u^{e}_{22}) + e_{33}u_{33}, \\
\sigma_{11}^{e} = c_{11}^{e}u_{11}^{e} + c_{12}^{e}u_{22}^{e} + c_{13}^{e}u_{33}^{e} - e_{31}E, \\
\sigma_{22}^{e} = c_{12}^{e}u_{11}^{e} + c_{11}^{e}u_{22}^{e} + c_{13}^{e}u_{33}^{e} - e_{31}E, \\
\sigma_{33}^{e} = c_{13}^{e}(u_{11}^{e} + u_{22}^{e}) + e_{33}^{e}u_{33} - e_{33}E, \\
H^m = a^mM + b^mM^3 + c^mM^5 - 2(q_{31}(u_{11} + u_{22}) + q_{33}u_{33})M, \\
\sigma_{11}^{m} = c_{11}^{m}u_{11}^{m} + c_{12}^{m}u_{22}^{m} + c_{13}^{m}u_{33}^{m} - q_{31}M^2, \\
\sigma_{22}^{m} = c_{12}^{m}u_{11}^{m} + c_{11}^{m}u_{22}^{m} + c_{13}^{m}u_{33}^{m} - q_{31}M^2, \\
\sigma_{33}^{m} = c_{13}^{m}(u_{11}^{m} + u_{22}^{m}) + e_{33}^{m}u_{33}^{m} - q_{33}M^2.
\end{cases}
$$

(2)

When writing the system of equations (2), the Voigt notation [6] is used for convenience. The plate is considered free, i.e. the components of the stress tensor must go to 0 at plate borders

$$
\sigma_{11}|x=\pm A/2 = 0, \quad \sigma_{22}|y=\pm B/2 = 0, \\
\int_{-h}^{h_m} \sigma_{11} dz = 0, \quad \int_{-h}^{h_m} \sigma_{22} dz = 0.
$$

(3)

The components of the displacement vector $u_i$ and the stress tensor $\sigma_{ij}$ must be continuous at the interface between the layers. The last boundary conditions in (3) mean that the total force acting on the plate [6] is zero. Since the plate is thin, the Love-Kirchhoff theory [6] is applicable to its description. In accordance with this theory, we look for the solution of the elasticity problem (2),(3) in the form of series in powers of $z$ and restrict ourselves only to the main terms

$$
u_1(x, y, z) = u(x, y), \\
u_2(x, y, z) = v(x, y), \\
u_3(x, y, z) = zw(x, y).
$$

(4)

The functions $u(x, y)$ and $v(x, y)$ are the same for both layers due to the continuity of the displacements. For the function $w(x, y)$, the first condition in (3) implies the equality

$$
w = \frac{e_{33}}{c_{33}}E - \frac{c_{13}}{c_{33}}(u_{11} + u_{22}),
$$

(5)

that is, the values of $w(x, y)$ in the piezoelectric and magnetic layer may differ from each other. From the last conditions in (3), we obtain a system of linear equations for determining the unknowns $u_{11}$ and $u_{22}$, from which we express the components of the strain tensor through an electric and magnetic field
\[ u_{11} + u_{22} = \alpha E_e + \beta M_m^2, \]
\[ u_{33} = \frac{c_{33} - \alpha c_{13}}{c_{33}} E_e - \frac{c_{13}}{c_{33}} \beta M_m^2, \]  \( \text{(6)} \)

where the following notations are introduced
\[ \alpha = \frac{E_{13} h^e}{(C_{11} + C_{12}) h^e + (C_{11} + C_{12}) h^m}, \]
\[ \beta = \frac{Q_{13} h^m}{(C_{11} + C_{12}) h^e + (C_{11} + C_{12}) h^m}, \]
\[ C_{11} = c_{11} - \frac{c_{13}^2}{c_{11}}, \quad C_{12} = c_{11} - \frac{c_{13}}{c_{11}}, \]
\[ Q_{13} = q_{13} - \frac{c_{13} q_{33}}{c_{11}}, \quad E_{13} = e_{13} - \frac{c_{13} e_{33}}{c_{11}}. \]  \( \text{(7)} \)

The relations (6) include the known values of the electric field in the piezoelectric \( E_e \) and the magnetic field in the magnetic material \( M_m \). As a result of elimination of the elastic field, we obtain the final equation for determining the magnetization
\[ \frac{B}{\mu_0} = \hat{a} M + \hat{b} M^3 + c^m M^5, \]  \( \text{(8)} \)

where the constants \( k \) and \( b_0 \) have the form
\[ k = -2 \left( q_{31} \alpha + q_{33} \frac{c_{33} - \alpha c_{13}}{c_{33}} \right), \]
\[ b_0 = -2 \left( q_{31} - q_{33} \frac{c_{13}}{c_{33}} \beta \right). \]  \( \text{(9)} \)

Thus, the presence of the piezoelectric layer simply leads to a change in the Landau coefficients in the equation for determining the magnetization.

3. Results and discussion
A comparison was made with the results of the experiment [7] to check the dependence (8). \( \text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3 \) was chosen as the piezoelectric and \( \text{Fe}_{48}\text{Rh}_{52} \) as the magnetic material. An alternating magnetic field with a frequency of 0.4 Hz and a magnitude \( B=0.62 \text{T} \) was applied to the sample. Each layer had a thickness of 0.2 mm. The potential difference of the electric field was 25 V. Figure 2 shows the results of measuring the temperature hysteresis of the magnetization during heating and cooling regimes for the specified composite and the calculation using the formula (8). It is important to emphasize that for a complete description of the hysteresis the Landau-Khalatnikov differential equation should be used [8]
\[ \frac{\partial M}{\partial T} = \frac{B}{\mu_0} - \hat{a} M - \hat{b} M^3 - c^m M^5, \]  \( \text{(10)} \)

where the coefficient \( \tau \) characterizes the relaxation temperature of the magnetic layer. When calculating, the Landau coefficients were chosen from the best fit, by the least-squares criterion, of the experimental and theoretical curves and turned out to be \( \hat{a} = -739.49, \hat{b} = -0.0111 \text{ m/A}, \)
Figure 2. Comparison of the experimental temperature dependence of the magnetization of the FeRh/PZT composite at a magnetic field $B=T$ in the “heating-cooling” cycle with the theoretical curve (8).

$c = 0.103 \cdot 10^{-5} \text{m}^2/\text{A}^2$. As seen from the figure 2, both curves coincide well at temperatures from 300 to 325 K. Outside this temperature range, the experimental curves tends to the horizontal asymptote, and the theoretical one is unlimited. This means that the Landau model is unsuitable for large deviations from the temperature of the phase transition and it is necessary to use the Weiss model, which explains the presence of the saturation line of magnetization [9].

From the results obtained, it follows that for thin plates the magnetization does not depend on the shape of the plate, but is determined only by the thickness of its layers. This conclusion is valid for free samples. If the plate is fixed along the edge, then the method proposed in the work also allows one to find an equation for magnetization. However, the coefficients in new equation will include a dependence on the plate size. Also, the derived formula (8) allows finding the optimal ratio of plate thicknesses at which the magnetostrictive coefficient $k$ reaches the maximum value. One of the important results of the study is explicit expression for $k$. The magnetostrictive effect in the examined composite turned out to be linear in both the electric and magnetic fields. A change in the electric field, as follows from the equation (8), leads to a change in the temperature of the phase transition $T_m$ by the value of $kE_e$. This fact is experimentally confirmed: the shift of the magnetization curve is 3-5 K [7]. Note that if we take an BaTiO$_3$-type electrostriction material as the second layer, the change in $T_m$ will be quadratic in the electric field. If both piezoelectric and electrostrictive effects are taken into account, two magnetostrictive coefficients appear [7].

Thus, the electric field does not lead to an enhancement of $\mu CE$ in bilayer FeRh/PZT structure, but only allows it to be controlled. In contrast, the magnitude of electrocaloric effect in the PZT single layer can reach a significant value [10]. That is the enhancement technique reported in [11] is not relevant for $\mu CE$ in the case under study. It is well known that the synergistic interaction of various fields may lead to an increase in the phenomenon size, and $\mu CE$ can exceed individual components. However, the simultaneous use of two or more caloric effects allows raising the thermodynamic efficiency in a certain temperature range and under special conditions [12]. Such a finding can be used in the thermodynamic cycles of solid-state coolers. The main goal of the subsequent studies is to achieve such a ratio of the temperature of the phase transitions of the magnetic and electric phase by varying the additions to the multiferroic in such a way that mutual reinforcement of the $\mu CE$ main component terms (synergistic effect)
occurs. Also, to increase $\mu_{\text{CE}}$, a resonant amplification of the magnetoelectric coefficient $k$ can be employed during the excitation of elastic oscillations [13].

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