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THERMOMECHANICS OF MULTIFERROICS

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ABSTRACT. Generally understood ferroic media have been investigated by many authors. The majority of them have dealt with the electromagnetic nature of the domain structure of crystalline or amorphous solids. However, there exist also materials that have an internal ordered structure from the mechanical (elastic) point of view. They are called ferroelastics. The presentation proposes a thermomechanical model of irreversible and nonequilibrium processes that can run in continuous multiferroic media in which simultaneous interactions of various physical fields occur both in low and room temperatures. Attempts concerning a proposition of the constitutive theory resulting from linear and nonlinear forms of the free energy density are also presented.

1. Introduction

A ferroic crystal consists of two or more orientation states or domains. Under a particular driving force the anisotropic regions and/or domain walls move switching the crystal from one state to another. That process may be caused by elastic, electric and magnetic fields or even some combinations of them (Newnham 1974; Surowiak and Bochenek 2008). Ferroelectric, ferromagnetic and ferroelastic materials are examples of the so-called primary ferroic crystals. They characterize their orientation states: polarization, magnetization and strain. However, there are also materials, which change under driving forces their material properties like permittivities, susceptibilities, compliances and other characteristic coefficients. They are called as the secondary ferroic materials.

The primary ferroic class (Newnham 1974; Wadhawan 1984; Maugin 1988).

The **ferroelectrics** consist of domains or areas of ordered electric polarization.
The **ferromagnetics** consist of domains or areas of ordered magnetic polarization.
The **ferroelastics** have two or more orientation states of deformation.

The secondary ferroic class (Newnham 1974).

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The **ferrobielectricity** is a phenomenon arising from induced electric polarization field and/or the spontaneous one. Switching between orientation states occurs because of differences in the electric permittivity tensor.

The **ferrobimagnetism** occurs in media with the anisotropic magnetic susceptibility that can change under a magnetic driving force.

The **ferrobielasticity** takes place in crystals in which the elastic orientation states differ in elastic compliance (the four rank tensor) induced by the applied stress.

The **ferroelastoelectricity** is a cross-coupled ferroic phenomenon. The domain states of the ferroelastoelectricity differ in piezoelectric tensor. The crystal can be switched from one state to another when the electric field and the mechanical stress are applied simultaneously.

The **ferromagnetoelasticity** occurs in materials consisted of domains which differ in piezomagnetic coefficients. Therefore, the switching among domains is done by applying the mechanical stress and the magnetic field simultaneously.

The **ferromagnetoelectricity** is observed in materials in which the coupling between the electric and magnetic variables occurs. Moreover, if such magnetoelectric effects are different in various domains a polycrystal also behaves as a ferroic.

The multiferroics have an internal structure which, within the macroscopic and continuous model, is responsible for their specific physical properties. Very similar situation occurs in elastic media with negative Poisson's ratio called auxetics (Newnham 1974; Alderson and Evans 2001). Their internal structures in the form of chiral honeycombs, tetrachiral or hexachiral ones suggest that such small regions creating periodic or disordered symmetries can have also the character to direct. So that, they can form ferroic or multiferroic structures both isotropic and/or anisotropic ones.

The paper deals with the thermomechanical model of continuous multiferroic materials in which the elastic, thermal and electromagnetic fields may simultaneously interact. Since the auxetic properties and spontaneous features of the above materials might to be taken into account altogether the specific form of the Gibbs free enthalpy is proposed.

2. Thermodynamical model of interactions

In this Section we model physical processes and interactions listed in Introduction. That model concerns interactions among the elastic, thermal and electromagnetic fields in continuous media with specific internal structure (orientation elastic states, electric or magnetic spontaneous orientations and the cross-like effects that can occur in crystals also irradiated by neutrons which have magnetic moments - spins). The model is based on the irreversible extended thermodynamics. For the sake of simplicity only relaxation properties of the temperature field have been taken into account.

The state vector (set of independent variables) is assumed in the form (Maruszewski 1987; Maugin 1988; Maruszewski 1993; Restuccia and Maruszewski 1998):

$$\mathscr{C} = \{\sigma_{ij}, \mathscr{E}_i, B_i, T, q_i, \Gamma_{ij}^{\alpha,\beta}, \eta_i\}. \tag{1}$$

σ_{ij} is the stress tensor, $\mathscr{E}_i$ is the electric field intensity and B_i is the magnetic induction in the moving frame, T is the temperature, q_i is the heat flux, $\Gamma_{ij}^{\alpha\beta}$ is the anisotropy-grain tensor (Maruszewski 1993) and η_i is the magnetic moment density of the neutron field (Maugin and Maruszewski 1989):

$$\Gamma_{ij}^{\alpha\beta}(x_k,t) = V^{\alpha} n^{\alpha\beta}(x_k,t) A^{\beta\gamma}, \tag{2}$$

where V^{α} denotes the characteristic dimension of α-grain or domain, $n^{\alpha\beta}(x_k,t)$ is the number density of the α-grain or domain field possessing β anisotropy. Since $A^{\beta\gamma}$ deals only with the spontaneous strain, the tensor $\Gamma_{ij}^{\alpha\beta}$ may be regarded as a generalization of the order parameter that has been used in description of ferroelastic phenomenon by Landau. Such parameters as well as η_i within the thermodynamical model are treated as the internal variables.

All the processes occurring in materials in which the above interactions may take place are governed by (we have neglected the transport of eventually existing electric charges):

– *the continuity equation*

$$\dot{\rho} + \rho v_{i,i} = 0, \tag{3}$$

where ρ is the mass density and v_i is the velocity of the body point,

– *the momentum balance*

$$\rho \dot{v}_i = \sigma_{ji,j} + \mathscr{E}_k P_{k,i} + B_{i,j} M_j + f_i, \tag{4}$$

where f_i is the body force, P_i is the polarization and M_j is the magnetization,

– *the moment of momentum balance*

$$\varepsilon_{ijk}\sigma_{jk} + c_i(\eta_i, M_i) = 0, \tag{5}$$

where c_i is the moment of momentum coming from the neutron field and other magnetizations,

– *the internal energy balance*

$$\begin{aligned} \rho \dot{e} &= \sigma_{ji} v_{i,j} - M_i \dot{B}_i + \rho \mathscr{E}_i \dot{\mathscr{P}}_i - q_{i,i} + \rho r, \\ P_i &= \rho \mathscr{P}_i, \end{aligned} \tag{6}$$

where e denotes the internal energy density,

– *the Maxwell equations*

$$\begin{aligned} \varepsilon_{ijk} E_{k,j} &= -\frac{\partial B_i}{\partial t}, \quad \varepsilon_{ijk} H_{k,j} = \frac{\partial D_i}{\partial t}, \\ D_{k,k} &= 0, \quad B_{k,k} = 0, \end{aligned} \tag{7}$$

where D_k is the electric induction and H_k is the magnetic field intensity,

– *the evolution equations of internal variables*

$$q_i^* = Q_i(\mathscr{C}), \tag{8}$$

$$\Gamma_{ij}^{*\alpha\beta} = G_{ij}^{\alpha\beta}(\mathscr{C}), \tag{9}$$

$$\eta_i^* = N_i(\mathscr{C}), \tag{10}$$

where superimposed dot denotes the material time derivative and superimposed star denotes the Zaremba-Jaumann time derivative,

– *the entropy inequality*

$$\rho\dot{S}+\phi_{k,k}-\frac{\rho r}{T}\geq 0, \tag{11}$$

where S is the entropy density, ϕ_k is the entropy flux. In the sequel we confine the electromagnetic properties only to piezoelectric and piezomagnetic phenomena within the primary and secondary ferroic classes. So, we neglect the neutron irradiation influences on the considered processes. Therefore, we assume that (Maugin and Maruszewski 1989):

$$D_i=\varepsilon_0(\delta_{ij}+\kappa_i)\mathscr{E}_j, \quad B_i=\mu_0(\delta_{ij}+\chi_{ij})H_j, \tag{12}$$

where κ_{ij} is the electric permittivity and χ_{ij} is the magnetic susceptibility. We have omitted the influence of the neutron magnetic moment assuming that $\eta_i \ll M_i$ in $B_i = \mu_0(H_i+M_i+\eta_i)$ (note that $P_i=\kappa_{ij}\mathscr{E}_j, M_i=\chi_{ij}H_j$).

The constitutive relations (link between the model and real processes in materials) are based on the internal energy balance, Eqn. (6), and the entropy inequality, Eqn. (11). From them there result the following relations knowing that the enthalpy, free enthalpy and the kinetic potential vector read (Maruszewski 1987; Maugin and Maruszewski 1989; Restuccia and Maruszewski 1998):

$$\begin{aligned} h &= e-\frac{1}{\rho}\sigma_{ij}\varepsilon_{ij}, \quad G=h-TS, \\ L_k &= \rho v_k G - T\phi_k. \end{aligned} \tag{13}$$

From Eqns. (13) with the use of Eqns. (1), (3) - (10) and inequality (11) we obtain

$$\begin{aligned} \varepsilon_{ij} &= -\frac{\partial G}{\partial \sigma_{ij}}, \qquad S=-\frac{\partial G}{\partial T}, \quad \frac{\partial G}{\partial T_{,i}}=0 \\ M_i &= -\rho\frac{\partial G}{\partial B_i}, \qquad P_i=-\rho\frac{\partial G}{\partial \varepsilon_i} \\ \gamma_{ij}^{\alpha\beta} &= \rho\frac{\partial G}{\partial \Gamma_{ij}^{\alpha\beta}}, \qquad \frac{\partial L_k}{\partial q_i}=\delta_{ik}+\rho\frac{\partial G}{\partial q_i}v_k \\ \frac{\partial L_k}{\partial \varepsilon_i} &= -v_k P_i, \qquad \frac{\partial L_k}{\partial B_i}=-v_k M_i \end{aligned} \tag{14}$$

and the residual inequality from which the remaining part of the kinetic constitutive relations result ($\gamma_{ij}^{\alpha\beta}$ denotes the chemical-like potential related to the anisotropy-grain tensor). Hence the Gibbs free energy is presented in the form

$$G=G_1+G_2+G_3 \tag{15}$$

where (Newnham 1974; Maruszewski 1987, 1993; Restuccia and Maruszewski 1998; Giambò *et al.* 2002)

$$\begin{aligned} G_1 &= G_1(\sigma_{ij},\mathscr{E}_i,B_i,T,q_i) \\ G_2 &= \Gamma_{ij}^{\alpha\beta}\sigma_{ij}+P_i^s\mathscr{E}_i+M_{ij}^sH_i \\ G_3 &= \frac{1}{2}s_{ijkl}^s\sigma_{ij}\sigma_{kl}+\frac{1}{2}\kappa_{ij}^s\mathscr{E}_i\mathscr{E}_j+\frac{1}{2}\chi_{ij}^sH_iH_j+ \\ &\quad +d_{ijk}^s\mathscr{E}_i\sigma_{jk}+l_{ijk}^sH_i\sigma_{jk}+\alpha_{ij}^sH_i\mathscr{E}_j \end{aligned} \tag{16}$$

where G_1 concerns nonferroics, G_2- primary ferroics and G_3 - secondary ferroics. In this way, using Eqns. (14) and (15), the formulation of a suitable constitutive theory is possible. The superscript s denotes spontaneous effects. Please note that making the elastic part of G_1 and compliance s^s_{ijkl} in G_3 dependent on Youngs's modulus and Poisson's ratio opens the possibility to consider auxetic mulitiferroics.

Remark, that there exist several ways for a proper analysis and presentation of the constitutive theory based on Eqns. (1) - (10), (13) - (16). The mathematical methods to determine the exact forms of the constitutive relations Eqn. (14) based on Eqns. (15), (16) come always from the exploitation of the entropy inequality Rel. (11) (Maruszewski 1987; Maugin and Maruszewski 1989; Restuccia and Maruszewski 1998). One of the two main such methods is based on the suitable expansions of the potentials Eqns. (13), (15) with respect to Eqn. (1) into Taylor's series and finally the use of Eqns. (14) (Maruszewski 1981). Next the analysis of the residual inequality coming from Rel. (11) with the help of Onsager - Casimir's kinetic relations (Maruszewski 2008b) gives their proper and exact forms. The second method of the proper formulation of the constitutive theory is the analysis of the entropy inequality, Rel. (11), by the use of Liu's theorem related to Eqns. (3) - (10) and inequality (11) (Liu 1972; Restuccia and Maruszewski 1997), and the formulation of Eqns. (14) with the help of their proper polynomial representations in the quantities of Eqn. (1) (Smith 1971; Maruszewski 2008a).

3. Conclusions

The presented thermomechanical model of interactions makes possible a description of multiferroics of a reasonable wide electro-magneto-thermo-mechanical properties. Particularly, the model allows to consider materials of specific mechanical properties formulating the Gibbs free energy in its elastic part in different nonlinear forms like Murnaghan's, Blatz-Ko's, Mooney's, Treloar's and others which can take into account higher order mechanical nonlinearities (Samsonov 2001). On converting the mechanical coefficients into the Young's modulus and Poisson's "language" allows also to consider auxetic materials whose physical nature seems to be close to a nature of multiferroics.

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References

Alderson, A. and Evans, K. E. (2001). "Rotation and dilatation deformation mechanisms for auxetic behaviour in the α-cristobalite tetrahedral framework structure". *Physics and Chemistry of Minerals* **28**, 711–718. DOI: 10.1007/s002690100209.

Giambò, S., Maruszewski, B. T., and Restuccia, L. (2002). "On a nonconventional thermodynamical model of a defective piezoelectric crystal". *Journal of Technical Physics* **43**, 155–163.

Liu, I. S. (1972). "Method of Lagrange multipliers for exploitation of the entropy principle". *Archive for Rational Mechanics and Analysis* **46**, 131–148. DOI: 10.1007/BF00250688.

Maruszewski, B. T. (1981). "Dynamical magnetothermoelastic problem in circular cylinders I. Basic equations". *International Journal of Engineering Science* **19**, 1233–1240. DOI: 10.1016/0020-7225(81)90143-9.

Maruszewski, B. T. (1987). "Coupled evolution equations of deformable semiconductors". *International Journal of Engineering Science* **25**, 145–153. DOI: 10.1016/0020-7225(87)90002-4.

Maruszewski, B. T. (1993). "On an anisotropy - grain tensor". *Physica Status Solidi (b)* **178**, 265–279. DOI: 10.1002/pssb.2221780202.

Maruszewski, B. T. (2008a). "A stress field in the vortex lattice in the type - II superconductor". *Atti dell'a Accademia Peloritana dei Pericolanti. Classe di Scienze Fisiche, Matematiche e Naturali* **86**, C1S0801014 (1), 1–12. DOI: 10.1478/C1S0801014.

Maruszewski, B. T. (2008b). "On nonlinear kinetic effects in the vortex array in superconductors". *Journal of Mechanics of Materials and Structures* **3**, 1105–1111. DOI: 10.2140/jomms.2008.3.1105.

Maugin, G. A. (1988). *Continuum mechanics of electromagnetic solids*. Amsterdam: North-Holland. DOI: 10.1002/zamm.19890691106.

Maugin, G. A. and Maruszewski, B. T. (1989). "Equations of neutron transport through deformable paramagnets". *Journal of Non - Equilibrium Thermodynamics* **14**(4), 385–396. DOI: 10.1515/jnet.1989.14.4.385.

Newnham, R. E. (1974). "Domains in minerals". *American Minearologist* **59**, 906–918. URL: rruff.info/doclib/am/vol59/AM59_906.pdf.

Restuccia, L. and Maruszewski, B. T. (1997). "On a form of the stress tensor in a heterogeneous and anisotropic nonlinear thermoelastic solid". *Journal of Technical Physics* **38**, 711–717.

Restuccia, L. and Maruszewski, B. T. (1998). "Nonlinear thermoelasticity of ferroelastics". *Mechanics Research Communications* **25**, 137–145. DOI: 10.1016/S0093-6413(98)00017-2.

Samsonov, A. M. (2001). *Strain solitons in solids and how to construct them*. Monographs and Surveys in Pure and Applied Mathematics 117. New York: Chapman & Hall/CRC.

Smith, G. F. (1971). "On isotropic functions of symmetric tensor, skew - symmetric tensor and vector". *International Journal Engineering Science* **9**, 899–916. DOI: 1016/0020-7225(71)90023-1.

Surowiak, Z. and Bochenek, D. (2008). "Multiferroic materials for sensors, transducers and memory devices". *Archives of Acoustics* **33**(2), 243–260. URL: http://acoustics.ippt.gov.pl/index.php/aa/article/view/531/pdf_237.

Wadhawan, V. K. (1984). "Ferroelasticity". *Bulletin of Materials Science* **6**(4), 733–753. DOI: 10.1007/BF02744001.

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