Physica B 443 (2014) 49–53

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Effect of coupling with strain in multiferroics on phase diagrams and elastic anomalies

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A R T I C L E I N F O

Article history:
Received 28 October 2013
Received in revised form
7 February 2014
Accepted 25 February 2014
Available online 4 March 2014

Keywords:
Multiferroics
Coupling with strain
Phase diagram
Phase transition temperature
Elastic modulus

A B S T R A C T

The Landau theory was applied to treat the phase diagrams for a multiferroic with two second order phase transitions taking into account the coupling of the primary order parameters with strain. Two order parameters are coupled biquadratically which corresponds to the magnetoelectric materials. The coupling with strain is assumed to be linear in strain and quadratic in order parameters. Three ordered phases are discussed. Analytic relationships were obtained for the phase transition temperatures and for elastic modulus changes through the phase transitions. Strong influence of the coupling with strain on the phase diagrams was shown.

1. Introduction

Recently, renewed attention was focused on multiferroic materials (single-phase and composite ones) because of their promising applications as multifunctional devices ([1,2] and references therein). The most interesting case is when two coupling order parameters are related to magnetic and electric orderings leading to the magnetoelectric effect. Experimental studies of multiferroic materials showed that their properties can be remarkably influenced by interaction with strains. Such an interaction becomes apparent, for instance, in elastic anomalies through the phase transitions [3–10] and in the impact of substrate-induced or epitaxial strain on the ferroic phase transitions and orientations of magnetic moments [11–13]. While much effort were made to reveal the role of strain in the multiferroic materials, some effects of coupling of the magnetic and electric order parameters with strain were still not discussed properly.

In the present paper we will theoretically describe how the coupling with strain affects the phase diagrams and the magnitudes of the order parameters of a multiferroic using the phenomenological Landau approach. The model can be applied to materials in which the multiferroic phase emerges as a result of two phase transitions occurring at different temperatures. This class of materials includes multiferroics with independent magnetic and ferroelectric subsystems such as borates, boracites, and some doped perovskites and also materials in which the same structural units are involved in magnetic and ferroelectric orderings such as hexagonal manganites or Bi and Pb perovskites [1,14]. Generally, the ferroelectric phase transition occurs in these multiferroics at temperatures higher than the magnetic one. The case of multiferroics in which ferroelectricity is generated by magnetic ordering is beyond our consideration.

The Landau theory was repeatedly applied to study the properties of multiferroic materials (see, for instance, Refs. [15,16]); however the treatment of the problem mentioned above was lacking. The precise expressions for the relevant elastic anomalies through the phase transitions will be also written for completeness, all the more because they were not derived for some particular cases until now.

2. Phase diagrams

Let us consider a multiferroic which has two successive phase transitions associated with two primary order parameters η and ξ. As we restrict our discussion to the most interesting case of magnetic and electric order parameters, the coupling between the order parameters takes the biquadratic form $(1/2)(\kappa\eta^2\xi^2)$ (κ is a phenomenological coupling constant). The magnetic order parameter for ferromagnetic materials can be equated to the magnetization while for the antiferromagnetics it can be identified with the difference in magnetizations of the magnetic sublattices. Additionally, we assume that both order parameters are coupled to strain ε which plays the

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http://dx.doi.org/10.1016/j.physb.2014.02.048
0921-4526

role of a secondary order parameter. While the phase diagram for the two coupled order parameters was considered repeatedly (see, for instance, Refs. [17,18]), its alterations caused by interaction with strain were never discussed. We will take into account the most important magnetoelastic coupling which is linear in strain (magnetostriction). Similarly, the electroelastic coupling is implied to be linear in strain and quadratic in spontaneous polarization (electrostriction). The latter means that the paraphase is centrosymmetric in agreement with the structure of known multiferroics [1,14]. Then the Landau free energy expansion for the second order phase transitions can be written as

$$\Phi=\tfrac{1}{2}\alpha\eta^2+\tfrac{1}{4}\beta\eta^4+\tfrac{1}{2}\kappa\eta^2\xi^2+\tfrac{1}{2}a\xi^2+\tfrac{1}{4}b\xi^4+\tfrac{1}{2}c\varepsilon^2+\tfrac{1}{2}\theta_1\varepsilon\eta^2+\tfrac{1}{2}\theta_2\varepsilon\xi^2, \tag{1}$$

where $\alpha=\alpha_0(T-T_1)$, and $a=a_0(T-T_2)$; α_0, a_0, β, b, c, θ_1, and θ_2 are phenomenological constants; α_0, a_0, β, and b are positive. We assume $T_2>T_1$.

The necessary conditions for Φ to have a local minimum at zero applied fields imply that the derivatives

$$\begin{cases}\frac{\partial\Phi}{\partial\eta}=\alpha\eta+\beta\eta^3+\kappa\eta\xi^2+\theta_1\varepsilon\eta\\ \frac{\partial\Phi}{\partial\xi}=a\xi+b\xi^3+\kappa\eta^2\xi+\theta_2\varepsilon\xi\\ \frac{\partial\Phi}{\partial\varepsilon}=c\varepsilon+\frac{1}{2}\theta_1\eta^2+\frac{1}{2}\theta_2\xi^2\end{cases} \tag{2}$$

are all equal zero (the equilibrium conditions). If we define for convenience

$$\tilde\beta=\beta-\frac{\theta_1^2}{2c},\quad \tilde b=b-\frac{\theta_2^2}{2c},\quad \kappa=\kappa-\frac{\theta_1\theta_2}{2c}, \tag{3}$$

the equilibrium conditions can be written using Eqs. (2) and (3) as

$$\begin{cases}\eta(\alpha+\tilde\beta\eta^2+\tilde\kappa\xi^2)=0\\ \xi(a+\tilde b\xi^2+\tilde\kappa\eta^2)=0\\ \varepsilon=-\frac{1}{2c}(\theta_1\eta^2+\theta_2\xi^2)\end{cases}. \tag{4}$$

System (4) leads to the emergence of four different phases depending on phenomenological parameters and temperature: the paraphase $\eta=0,\ \xi=0$; two different ordered phases $\eta=0,\ \xi\neq0$ and $\eta\neq0,\ \xi=0$; and the multiferroic phase $\eta\neq0,\ \xi\neq0$. The conditions of stability of these four phases can be found using the Hesse matrix

$$A=\begin{pmatrix}\frac{\partial^2\Phi}{\partial\eta^2} & \frac{\partial^2\Phi}{\partial\xi\,\partial\eta} & \frac{\partial^2\Phi}{\partial\varepsilon\,\partial\eta}\\ \frac{\partial^2\Phi}{\partial\eta\,\partial\xi} & \frac{\partial^2\Phi}{\partial\xi^2} & \frac{\partial^2\Phi}{\partial\varepsilon\,\partial\xi}\\ \frac{\partial^2\Phi}{\partial\eta\,\partial\varepsilon} & \frac{\partial^2\Phi}{\partial\xi\,\partial\varepsilon} & \frac{\partial^2\Phi}{\partial\varepsilon^2}\end{pmatrix}$$

$$=\begin{pmatrix}\alpha+3\beta\eta^2+\kappa\xi^2+\theta_1\varepsilon & 2\kappa\eta\xi & \theta_1\eta\\ 2\kappa\eta\xi & a+3b\xi^2+\kappa\eta^2+\theta_2\varepsilon & \theta_2\xi\\ \theta_1\eta & \theta_2\xi & c\end{pmatrix}. \tag{5}$$

A phase is stable when the Hesse matrix is positive definite. Then the free energy has a local minimum. To check whether the Hesse matrix is positive definite or not, one can use Sylvester's criterion. According to this criterion, the eigenvalues of a symmetric matrix are all positive if and only if all leading principle minors are positive. Let us consider the ranges of existence of different phases individually.

(a) **Paraphase** $(\eta=\xi=\varepsilon=0)$ **(phase 1).**
The Hesse matrix is diagonal with eigenvalues α, a, and c. It is positive definite if $T>T_2$.

(b) **Phase** $\eta=0,\ \xi\neq0$ **(phase 2).**
From system (4) the equilibrium values of the nonzero order parameters are given by $\xi^2=-a/\tilde b$ and $\varepsilon=a\theta_2/2\tilde bc$. This phase can exist below T_2. The Hesse matrix

$$A=\begin{pmatrix}\alpha-\frac{\tilde\kappa a}{\tilde b} & 0 & 0\\ 0 & 2b\xi^2 & \theta_2\xi\\ 0 & \theta_2\xi & c\end{pmatrix} \tag{6}$$

is positive when

$$\begin{cases}c>0\\ \det\begin{pmatrix}2b\xi^2 & \theta_2\xi\\ \theta_2\xi & c\end{pmatrix}>0\\ \det A>0\end{cases}. \tag{7}$$

The second inequality in system (7)

$$\det\begin{pmatrix}2b\xi^2 & \theta_2\xi\\ \theta_2\xi & c\end{pmatrix}=2c\tilde b\xi^2=-2ac>0 \tag{8}$$

is satisfied at $T<T_2$. The third inequality in system (7) becomes

$$\alpha-\frac{\tilde\kappa a}{\tilde b}>0 \tag{9}$$

which is satisfied at $0<T<T_2$ if $\tilde\kappa>\alpha_0\tilde bT_1/a_0T_2\equiv\tilde\kappa_1$ and at $0<\tilde T_{high}<T<T_2$ if $\tilde\kappa<\tilde\kappa_1$, where

$$\tilde T_{high}=T_2-\frac{T_2-T_1}{1-(a_0\tilde\kappa/\alpha_0\tilde b)}. \tag{10}$$

This means that the multiferroic phase may emerge only if $\tilde\kappa<\tilde\kappa_1$.

(c) **Phase** $\eta\neq0,\ \xi=0$ **(phase 3).**
From Eq. (4) we can find $\eta^2=-\alpha/\tilde\beta$ and $\varepsilon=\alpha\theta_1/2\tilde\beta c$. The former imposes T_1 as the upper temperature limit for phase 3. The Hesse matrix for phase 3 is

$$A=\begin{pmatrix}2\beta\eta^2 & 0 & \theta_1\eta\\ 0 & a-\frac{\tilde\kappa\alpha}{\tilde\beta} & 0\\ \theta_1\eta & 0 & c\end{pmatrix}. \tag{11}$$

One can show that the Hesse matrix (11) is positive definite within a temperature interval $0<T<\tilde T_{low}<T_1$ only if $\tilde\kappa>(a_0\tilde\beta/\alpha_0)(T_2/T_1\equiv\tilde\kappa_2)$, where

$$\tilde T_{low}=T_1-\frac{T_2-T_1}{\tilde\kappa\alpha_0/a_0\tilde\beta-1}. \tag{12}$$

Phase 3 does not exist if $\tilde\kappa<\tilde\kappa_2$. The temperature intervals where phases 2 and 3 exist, must not overlap for the second order phase transitions. This requires the additional condition $\tilde T_{low}\le\tilde T_{high}$ which is satisfied if

$$\tilde\kappa^2\le\tilde b\tilde\beta. \tag{13}$$

Inequality (13) imposes a restriction on the magnitude of the modified coupling constant $\tilde\kappa$ and can be denoted as the condition of the weak coupling.

(d) **Multiferroic phase** $\eta\neq0,\ \xi\neq0$ **(phase 4).**
For this phase the Hesse matrix is

$$A=\begin{pmatrix}2\beta\eta^2 & 2\kappa\xi\eta & \theta_1\eta\\ 2\kappa\xi\eta & 2b\xi^2 & \theta_2\xi\\ \theta_1\eta & \theta_2\xi & c\end{pmatrix}. \tag{14}$$

Sylvester's criterion gives the following inequalities:

$$\begin{cases}2\beta\eta^2>0\\ \det\begin{pmatrix}2\beta\eta^2 & 2\kappa\xi\eta\\ 2\kappa\xi\eta & 2b\xi^2\end{pmatrix}=4(\beta b-\kappa^2)\eta^2\xi^2>0\\ \det A>0\end{cases}. \tag{15}$$

The first inequality in (15) is obviously satisfied. The second one leads to $\kappa^2<\beta b$ which is the weak coupling condition