Ising-Like Model For Ferroelectric Phase Transitions In Tetragonal Tungsten Bronze Compounds

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Abstract : The two-component anisotropic Ising-like model was proposed to model the ferroelectric phase transitions in Tetragonal Tungsten Bronze (TTB) compounds. Using the mean-field approach we reconstructed the phase diagram of the TTB system and showed that depending on he relative strength of the interaction parameters there ferroelectric states are possible: (i) the state with y-directed polarization that corresponds to the tetragonal ferroelectric phase in TTB compounds, (ii) the state with x-directed polarization that corresponds to the orthorhombic TTB phase and (iii) the state with superposition of x- and y- polarization components that can correspond to the not yet discovered mixed phase.
Keyword: Ising model, Tetragonal Tungsten Bronze compounds, Ferroelectrics, Phase diagram.

I. Introduction

Last decades the ferroelectric Tetragonal Tungsten Bronze (TTB) type compounds have been extensively studied from both experimental and theoretical points of view. This interest is provided by the potential applications of their ferroelectric and nonlinear electro-active properties for developing of the new generation of non-volatile memories, detectors, sensors and nonlinear electronic switches [1–4]. The first ferroelectric TTB compound $K_{0.57}WO_3$ was discovered in 1949 [5]. Then, in 1953, the more smart ferroelectric TTB material - $PbNb_2O_6$ was synthesized [6]. In 1967 the non-linear optics properties on TTB crystals were investigated by IBM and Bell laboratories [7].

Unlike the most studied cubic perovskites the TTB compounds have the less symmetrical uniaxial tetragonal paraelectric phase with initial symmetry group 4/mmm. The great variety of TTB compounds is provided by the different possibilities of location of the metallic ions in the internal cavities, having the coordination numbers 15 (type A), 12 (type B) and 9 (type C), respectively. The ferroelectric properties of these materials depend strongly on the composition of the constituting elements. A weak variation of the composition could lead to notable change of the physical properties, such as the temperature and the order of transition. In particularly, it was discovered that the ferroelectric phase can be either of the tetragonal type with easy-axis spontaneous polarization or of the orthorhombic type with easy-plane spontaneous polarization. For example, for $Pb_{2(1-x)}Gd_xK_{1+x}Nb_5O_{15}$ (PGKN) compounds with $0 \leq x \leq 1$ the Para-Ferro transition was shown to be strongly depended of the rate of substitution of Gd [8,9].

In general, the tetragonal symmetry of ferroelectric phase with polarization **P** parallel to **c**-direction occurs mostly in the lead-free TTB-type compounds such as $K_3Li_2Nb_5O_{15}$ (T_c=430°C) [10]. The lead-containing compounds such as $Pb_2KNb_5O_{15}$ (T_c = 450 °C) [11-13] display generally an orthorhombic distortion in the provided by the strong polarizability of the Pb^{2+} ions that involve a structural anisotropy and distortion of oxygen octahedra [14]. Polarization, in this case, is perpendicular to the **c**-direction. Note, however, the special case of compound $PbK_2LiNb_5O_{15}$ (T_c=366°C) [15, 16], in which the ferroelectric phase is orthorhombic whereas the polarization is directed along axis c.

The objective of the present communication is to propose the theoretical model for explication of the reach phase diagram of TTB compounds in ferroelectric state. In Section 2 we shall propose the microscopic multi-component Ising-like model that incorporates the different inter-atomic interactions driving the ferroelectric transitions. This model will be studied by the mean field theory. In Section 3, we discuss the results and in Section 4 present the brief conclusion.

II. Formulations

In spite of the apparent simplicity of the Ising model and of the efforts of more than one generation of physicists, its exact solution is available for binary spin variable only in one- and two- dimensional case. In the

general case of multi-component spin variable and in three dimensional case only the approximate solution approaches are working. The simplest method that will be explored in the current publication for the formulated bellow model is the mean field approximation.

We consider an Ising model described by the Hamiltonian:

$$H=-J_x^a\sum_{\langle i,j\rangle}S_{i,j}^xS_{i+1,j}^x-J_x^b\sum_{\langle i,j\rangle}S_{i,j}^xS_{i+1,j}^x-J_y^a\sum_{\langle i,j\rangle}S_{i,j}^yS_{i,j+1}^y-J_y^b\sum_{\langle i,j\rangle}S_{i,j}^xS_{i,j+1}^x \quad (1)$$

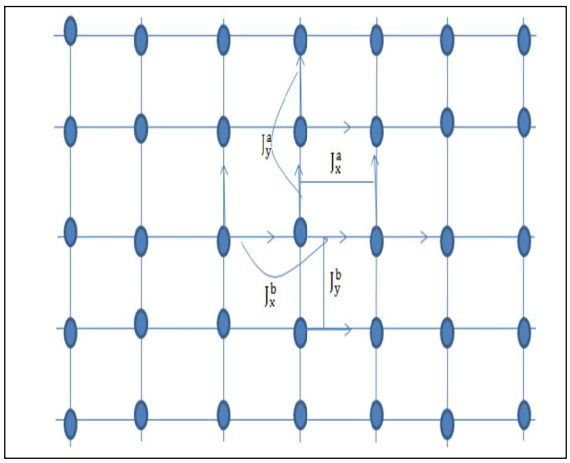

Figure 1: Network of multi-component TTB Ising model

where summation is given over the nearest neighbor sites only. As it is shown in Fig. 1, two types of interactions for each component P_i^x and P_i^y are distinguished. For the P_i^x components J_x^a is the interaction in the x direction and J_y^a is the interaction in the y-direction; for P_i^y components the interaction in the x direction is given by J_x^b whereas the interaction in the y direction is given by J_y^a.

We suppose to calculate the polarizations P_x and susceptibility of the system χ_x along the x direction and the corresponding values of P_y and χ_y along the y direction and determine the critical temperatures of possible transitions. Then, we shall trace the phase diagrams for different parameters of interaction: $R_1=\frac{J_x^b}{J_x^a}$; $R_2=\frac{J_y^b}{J_x^a}$ and $R_3=\frac{J_y^a}{J_x^a}$.

We shall use the mean field approach based on the variation of the free energy [17]:

$$F^{exact}\le F=Tr(\rho_0 H)+\frac{1}{\beta}Tr(\rho_0 Log(\rho_0 H)) \quad (2)$$

where F^{exact} and F are the exact and approximate free energies, and ρ_0 is a trial density matrix, trace *Tr* is performed over all spin configurations, and $\beta=1/K_BT$. The equality is provided when $\rho_0=e^{-\beta H}/Tr\,e^{-\beta H}$. Minimizing the right side of Eq.(2) for the most general density matrix that is factored into single density matrices we have $\rho_0=e^{-\beta H_0}/Tr\,e^{-\beta H_0}$, where H_0 is the mean field Hamiltonian:

$$H_0=-h_a\sum_{\langle i,j\rangle}P_{i,j}^x-h_b\sum_{\langle i,j\rangle}P_{i,j}^y \quad (3)$$

with

$$h_a=2P_x(1+R_3) \quad , \quad h_b=2P_y(R_1+R_2) \quad (4)$$

This can be written as

$$H_0=\sum_{\langle i,j\rangle}H_{0ij} \quad (5)$$

The thermal averages of P_i^x and P_i^y are given by:

$$\langle P_i^x\rangle=\frac{Tr(P_i^x e^{-\beta H_0})}{Tr(e^{-\beta H_0})} \text{ and } \langle P_i^y\rangle=\frac{Tr(P_i^y e^{-\beta H_0})}{Tr(e^{-\beta H_0})} \quad (6)$$

Calculating the traces: $Tr(P_i^x e^{-\beta H_0})$; $Tr(P_i^y e^{-\beta H_0})$ and $Tr(e^{-\beta H_0})$ we obtain the coupled self-consistent expressions for polarizations P_x and P_y:

$$P_x=\frac{\sinh(\beta h_a+\beta h_b)+\sinh(\beta h_a-\beta h_b)}{\cosh(\beta h_a+\beta h_b)+\cosh(\beta h_a-\beta h_b)} \quad (7)$$

and

$$P_y=\frac{\sinh(\beta h_a+\beta h_b)-\sinh(\beta h_a-\beta h_b)}{\cosh(\beta h_a+\beta h_b)+\cosh(\beta h_a-\beta h_b)} \quad (8)$$

III. Results and Discussions

To have the general idea about possible solutions of equations (7) and (8) we first take $R_2=0$; $R_3=1$ and vary R_1. The most general case of arbitrary interaction will be discussed elsewhere.

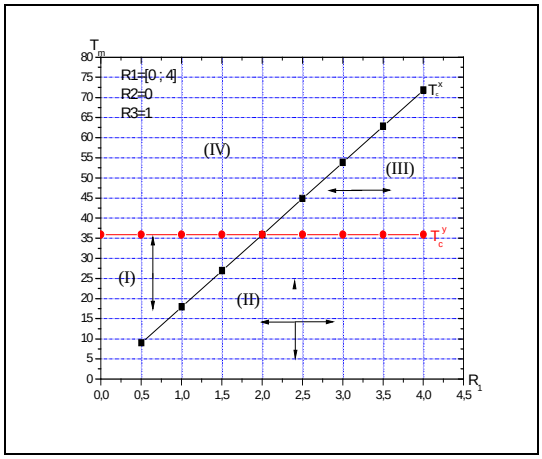

Figure 2: The phase diagram in $(T_m ; R_1)$ *plane for* $R_2 = 0$ *and* $R_3 = 1$

In Figure 2 we plot the $(T_c;R_1)$ phase diagram of the system, assuming $R_3=1$. This diagram shows the existence of four different regions: two regions (I) and (III) correspond to the absolutely stable ferroelectric phases with polarization ordering in x- and y-directions. Region (II) corresponds to the ferroelectric state where ordered x and y components of polarization coexist, and the region (IV) correspond to the disordered paraelectric state.

We also note that the critical temperature T_{cy} for the y-polarized phase is constant for all values of R_1 for the same values of R_2 and R_3. On the other side of phase diagram T_{cx} increases linearly with increasing of R_1.

For $J<2$, we observe the sequence of two phases. In the region II the ferroelectric phase is ordered along both x and y and in the region I the ferroelectric phase is ordered along x and disordered along y. In the region IV the spins are totally disordered and the phase corresponds to paraelectric state.

Now we present results when $R_2=0$ and R_1 and R_3 vary (Fig. 3).

The corresponding $(T_c;R_1)$ phase diagram is presented in Fig. 3. Let us note that now Tcy varies linearly with R_3 but Tmx is constant.

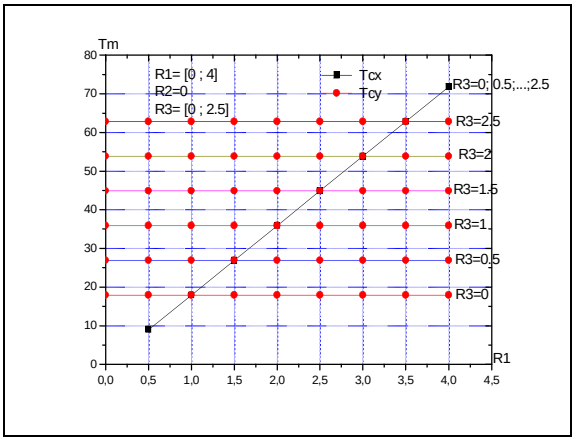

Figure 3: The phase diagram in $(T_m ; R_1)$ *plane for* $R_2 = 0$ *et* $R_3 \in [0; 2.5]$

IV. Conclusion

The influence of different microscopic interactions on phase diagram of a TTB ferroelectric material has been modeled by using the two-component anisotropic Ising-like model considered in the mean field approximation. We have found that for interaction parameters $R_2=0$ and $R_3=1$ the phase diagram consists from two regions corresponded to the absolutely stable ferroelectric phases with x- and y- polarization and from the region corresponded to the disordered paraelectric state. For another choice of interaction parameters: $R_2=0$ and $R_3 \in [0;2.5]$ we have show that Tcy varies linearly with R_3 but Tmx is constant.

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V. References

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