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Research paper

Landau theoretical analyses of phase transitions and ferroelec-tricity in antiferroelectric ferroics

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Abstract

This paper presents Landau theoretical interpretation of phase transitions in Antiferroelectrics (AFEs) materials. The results show that the phase transitions occurring in AFEs have prominently first and second order properties. Landau theories of first and second order phase transition have been appropriately analyzed in order to explain some of desirable phenomenological behaviors occurring in AFE materials. The spatial order parameter profile of AFE domain wall was derived and tested for possibilities of having ferroelectricity (FE) in accordance with Landau type energy functional. It was found that FE may appear but with additional system instability because of additional energy as a result of polarization gradient.

Keywords: *Antiferroelectrics; Domain Walls; Ferroelectricity; Ferroics; Phase Transitions.*

1. Introduction

By definition, ferroics represent classes of materials whose properties are mainly derived from the crystallographic and physical properties of their structural phase transitions. This group of materials typically cover large area of functional materials such as ferromagnetics, antiferromagnetics and non-magnetics together with their static and dynamic properties. Some groups of non-magnetic ferroics such as ferroelectrics (FEs) present most of the interesting device functioning properties such as high dielectric susceptibility, hysteresis, electro-mechanical coupling, electro-optical effects, memory effects and electrical displacements. Ferroics also form a group of important material candidates for domain and domain-wall engineering. Besides being good candidates for domain wall engineering, some ferroics, particularly lead-free ferroics present powerful tool for the development of environmental friendly FEs and piezoelectric materials [1], [2], [3]. Such materials are used in a wide range of technological devices and components. These include applications as sensors, transducers and actuators that are integrated in a variety of multifunctional technologies ranging from biomedical instrumentation to energy structures, communication and information storage systems.

Antiferroelectric (AFE) ferroics are defined by spontaneous neighboring dipoles of ions in their crystal structures. These dipoles are lined up in antiparallel directions to each other so that in high temperature phases the net spontaneous macroscopic polarization of the crystal as a whole becomes zero [4]. To be classified as FE ferroics a material needs to possess more than one stable polarization orientation states in the absence of electric field and mechanical stress but the states can be reoriented in one of its states by means of applied electric field, stress or combination of the two. FE materials, therefore manifests themselves by the huge peak in dielectric permittivity at the phase transition temperature [5]. This is because at the transition temperature (T_c) when the temperature, T equals T_c, the dielectric permittivity becomes infinitely large in agreement with Landau definition of the dielectric constant that is based on Curie-Weiss formula. This is given by:

$$\varepsilon_{T_C} = \frac{1}{\alpha_0 (T - T_C)} \tag{1}$$

Conversely, huge dielectric peaks do not appear at the phase transition of AFE materials [5] [6]. In these materials, FE is suppressed by the AFE structural order parameter η expressed in equation 2.

$$\varepsilon_{T_C} = \frac{1}{\alpha_0 (T - T_C) + \gamma\eta^2} \tag{2}$$

In terms of structural depiction, the two dipoles of AFE materials are described generally by two different order parameters, P and η. Consequently, as a result of temperature induced phase transitions and symmetry breaking, the pairing that occurs between these structural order parameters can lead to the phase transition with only one of the them active [7]. These structural changes can in principle lead to most of the important physical properties such as FE occurring in AFE materials. For example, it is interesting to learn how the local order parameters near domain walls react to the structural coupling phenomena [7]. It was hypothesized by these authors [7] that because of order parameter coupling inside the AFE domain wall, in regions where the local order parameter (η) becomes zero; FE can be favored.

However, understanding of phases and domain wall structures by either theoretical or experimental treatment of ferroics especially in AFE materials had never been trivial and present very huge challenges. Due to these challenges, Landau theoretical investigation of ferroics features have received considerable attention in the literature [8], [9], [10], [11], [12]. It is against this background that, this paper attempts to study theoretically the characteristics of AFE ferroics. The paper presents some insights on theoretical interpretation of phase transitions and domain walls in perovskite

AFE ferroics. Landau type theory that is based generally on Gibbs free energy is used to investigate the important phenomenological conditions such as the critical transition temperature points, T*, for which, AFE materials can develop FE behaviours. It is shown that, the order parameter coupling can lead to shifting of transition temperature that ultimately suggests the appearance of FE in the local region of AFE domain walls.

2. Phase transitions in AFE ferroics

Historically, an initiate work on the development of AFE phenomenological theory for both first and second order phase transitions was reported in 1951 by Kittel [13]. Based on Kittel's work, in a low temperature phase the AFE dipole moments might not be perfectly compensating each other [4]. In such a situation the unit cell of AFE state may acquire non-zero net dipole moments and the free energy density ΔQ for the first order phase transition theory of AFE was proposed [4]. It is given by:

$$\begin{aligned} Q(P_m, P_n, T) &= Q_0 + f(P_m^2 + P_n^2) \\ &+ gP_mP_n + h(P_m^4 + P_n^4) + i(P_m^6 + P_n^6) \end{aligned} \tag{3}$$

Where P_m and P_n are polarization states arising from the two identical inter-dispersed atoms or unit cells of a given AFE crystal structure with two identical lattices m and n. The letters f, g, h and i are temperature dependent energy expansion coefficients [4]. Accordingly, for the second order phase transition, ΔQ is written in form of expanded Helmholtz's free energy per unit volume. This is given by:

$$\begin{aligned} Q(P_m, P_m, T) &= Q_0 + f(P_m^2 + P_n^2) \\ &+ gP_mP_n + h(P_m^4 + P_n^4) \end{aligned} \tag{4}$$

Based on these phase transition energy functions, it is possible to obtain expressions for the spontaneous polarization P_m and P_n at given temperatures. This is possible since at given phase transition temperatures, $\partial \Delta Q / \partial P_m = 0$ and $\partial \Delta Q / \partial P_n = 0$ [14]. For example, the AFE-FE transition temperatures T_C can also be determined from $P_m(T_C) = 0$ and $P_n(T_C) = 0$ [14]. Taking the transition cases of first and second order under the conditions of zero stress and zero external electric field, spontaneous polarization states can be deduced in much the same way as in ordinary FE phase transitions reported elsewhere [15], [16], [17], [18], [19]. For example, the minimization of free energy density (equation 3) leads to:

$$\partial(\Delta Q)/\partial P_m = 2fP_m + gP_n + 4hP_m^3 + 6iP_m^5 = 0 \tag{5a}$$

$$\partial(\Delta Q)/\partial P_n = 2fP_n + gP_m + 4hP_n^3 + 6iP_{nb}^5 = 0 \tag{5b}$$

Solving equation (5) for spontaneous polarizations in first order phase transitions, one arrives at:

$$\begin{aligned} &6i(P_n^2)^2 + 4hP_n^2 + (2f + g) \\ &= 6i(P_m^2)^2 + 4hP_m^2 + (2f + g) = 0 \end{aligned} \tag{6a}$$

Such that $P_{sm} = -P_{sn}$ with:

$$|P_{sm}| = \left(\frac{-2h \pm \sqrt{4h^2 - 6i(2f + g)}}{6i} \right)^{1/2} \tag{6b}$$

Similarly, the second order energy equation 4 is treated for its minimum energy density at equilibrium. This leads to:

$$\partial(\Delta Q)/\partial P_m = 2fP_m + gP_n + 4hP_m^3 = 0 \tag{7a}$$

$$\partial(\Delta Q)/\partial P_n = 2fP_n + gP_m + 4hP_n^3 = 0 \tag{7b}$$

Solving equation (7) for AFE second order spontaneous polarizations P_{sm} and P_{sn} gives:
$P_{sm} = -P_{sn}$ With:

$$|P_{sm}| = \sqrt{(2f + g)/-4h} \tag{8}$$

Note that for structural stability reasons h is positive (h>0) and depends on the sign of g such that the system can switch between FE and AFE phases transitions depending on the relative sizes of f and h.

2.1. AFE-FE phase transitions

The alternative definition of AFE materials describes them to be antipolar crystals with free energies that are closely comparable to those of FE or close modification of their crystal structures [20]. Based on this definition it was suggested that the free energies of some AFE phases are very similar to FE phases to the extent that they usually switch from AFE to FE structures. This is in principle true based on equation 8. The driving forces of such switching being some physical forces such as external field or mechanical stress [20] and temperature for the case of ferroics. It was also shown earlier [14] that by including a cross term of fourth order of the form $P_I^2 P_{II}^2$ which is obtained generally from linear combinations [21] of P_m and P_n such that: $P_{II} = P_m + P_n$ and $P_{II} = P_m - P_n$. The Landau-Kittel expression of Q can be used to describe the AFE-FE phase transitions. In fact, the AFE-FE thermodynamic transition can be attributed to the instability of the AFE structures at low temperatures below Curie points.
To begin with, one follows the argumentation from Charnaya et al. [21] in which AFE first and second order phase transitions can be interpreted based on basic vector notation of polarization states P_m and P_n. This gives:

$$P_m = \frac{P_I + P_{II}}{2} \tag{9a}$$

$$P_n = \frac{P_{II} - P_I}{2} \tag{9b}$$

When equations (4) and (9) are added the energy density of second order phase transition in AFE is obtained. It is:

$$\begin{aligned} \Delta Q = f\left(\left(\frac{P_I + P_{II}}{2} \right)^2 + \left(\frac{P_{II} - P_I}{2} \right)^2 \right) + g\left(\left(\frac{P_I + P_{II}}{2} \right)\left(\frac{P_{II} - P_I}{2} \right) \right) \\ + h\left(\left(\frac{P_I + P_{II}}{2} \right)^4 + \left(\frac{P_{II} - P_I}{2} \right)^4 \right) \end{aligned} \tag{10a}$$

Or equivalently as,

$$\begin{aligned} \Delta Q &= \frac{f}{2}(P_I^2 + P_{II}^2) + \frac{g}{4}(P_I^2 - P_{II}^2) \\ &+ \frac{1}{16}h(P_I^4 + P_{II}^4 + 6P_I^2P_{II}^2 + P_I^2 + P_{II}^2 + 6P_I^2P_{II}^2) \end{aligned} \tag{10b}$$

Equation (10b) simplifies further to give

$$\begin{aligned} \Delta Q &= \frac{1}{2}\left(f - \frac{g}{2} \right)P_{II}^2 + \frac{1}{2}\left(f + \frac{g}{2} \right)P_I^2 \\ &+ \frac{1}{8}h(P_I^4 + 6P_I^2P_{II}^2 + P_{II}^4) \end{aligned} \tag{10c}$$

Up to this point the Curie-Weiss formula can be used to introduce the temperature dependence of the energy density. The term $(f - g/2)$ can be replaced from equation 10c by the linear temperature dependence of phase transitions [21] according to Curie-Weiss law such that:

$$\alpha = (f - g/2) = \alpha_0 (T - T_C) \tag{11}$$

As for the case of FE phase transitions the Curie phenomenological factor is here expressed in a usual way such that $\alpha_0 (T > T_C) > 0$. Using equations 11 and 10c one arrives at a relationship that can be used for studying the temperature induced phase transitions in AFE particularly for the AFE-FE phenomena. It is expressed as:

$$\begin{aligned} \Delta Q &= \frac{1}{2}\alpha_0 (T - T_C) P_{II}^2 + \frac{1}{2}(\alpha_0 (T - T_C) + g) P_I^2 \\ &+ \frac{1}{8} h (P_I^4 + 6 P_I^2 P_{II}^2 + P_{II}^4) \end{aligned} \tag{12}$$

Therefore, it can be reasoned that at low temperatures that are lower than T_C an AFE-FE phase transition can occur. This can be confirmed by means of Landau theory. As proposed by Benguigui [14] one considers the free energy which has stable minimum for either of the polarization states. If for example the infinite polarization conditions of the system is considered [21] logistically one sets $P_m = P_n$, prompting to $P_I = 0$, since $P_I = P_m - P_n$ and equations 13 and 14 can be obtained from equation 12.

$$\Delta Q = \frac{1}{2}\alpha_0 (T - T_C) P_{II}^2 + \frac{1}{8} h P_{II}^4 \tag{13}$$

$$\partial(\Delta Q)/\partial P_{II} = \alpha_0 (T - T_C) P_{II} + \frac{1}{2} h P_{II}^3 = 0 \tag{14}$$

Spontaneous polarization can now be easily evaluated by obtaining explicit polarization expression from equation 14, it is written as:

$$P_{sII} = \sqrt{\frac{-2\alpha_0 (T - T_C)}{h}} \tag{15}$$

Similar theoretical approach can be used for investigating the possibility of occurrences of spontaneous polarization during first order phase transitions occurring in AFE materials. In this case everything works similar as in second order except the last term in equation 3 which can be expanded and written as:

$$\begin{aligned} i(P_m^6 + P_n^6) &= i(P_I^4 + P_{II}^4 + 4 P_I P_{II}^3 + 4 P_I^3 P_{II} \\ &+ 6 P_I^2 P_{II}^2)^2 + i(P_I^4 + P_{II}^4 - 4 P_I P_{II}^3 - 4 P_I^3 P_{II} + 6 P_I^2 P_{II}^2)^2 \end{aligned} \tag{16}$$

This simplifies further to:

$$\begin{aligned} & i(P_m^6 + P_n^6) \\ &= \frac{1}{32} i(P_I^6 + P_{II}^6 + 70 P_I^4 P_{II}^4 + 28 P_I^6 P_{II}^2 + 28 P_I^2 P_{II}^6) \end{aligned} \tag{17}$$

Adding the two equations 13 and 17 gives the relationship for the AFE first order temperature phase transitions. This is written as follows

$$\begin{aligned} \Delta Q &= \frac{1}{2}\alpha_0 (T - T_C) P_{II}^2 + \frac{1}{2}(\alpha_0 (T - T_C) + g) P_I^2 \\ &+ \frac{1}{8} h (P_I^4 + 6 P_I^2 P_{II}^2 + P_{II}^4) \\ &+ \frac{1}{32} i(P_I^6 + P_{II}^6 + 70 P_I^4 P_{II}^4 + 28 P_I^6 P_{II}^2 + 28 P_I^2 P_{II}^6) \end{aligned} \tag{18}$$

Assuming that FE phase occurs and using similar approach as in second order phase transition with $P_{I\infty} = 0$, one arrives at:

$$\Delta Q = \alpha_0 (T - T_C) P_{II}^2 + \frac{1}{4} h P_{II}^4 + \frac{1}{16} i P_{II}^6 \tag{19}$$

Solving equation 19 for P_{II} at static conditions results to the relationship for the first order spontaneous polarization in AFE, it is written as:

$$P_{sII}^2 = \frac{-h \pm \sqrt{h^2 - 8i(\alpha_0 (T - T_C))}}{2i} \tag{20}$$

Although it is not easily known whether the low temperature AFE phases are polar or not, it can be stated that FE can usually occur in particular AFE phase transitions. This is in agreement with Landau theory basing on equation 15 for second order and equation 20 for first order. This depends on temperature and on the value of Landau phenomenological expansion coefficients h and i. To be sure of which transition is occurring as can be suggested by experiments at particular temperatures, one can work further with the same Landau theory to interpret and confirm the phase transition at critical points as either continuous (second order) or discontinuous (first order). An example has been shown already in AFE ceramics of La-doped PZT by Barranco-Pelàiz and coworkers [20].

3. FE in AFE domain wall

The Landau-Kittel theory of AFE can in general be used to describe many properties of AFE systems. For example, the second order expression 3 can be rewritten more conveniently for the purpose of understanding special domain walls in AFE ferroics. In terms of order parameter, η for P_{II} and P for P_I, the second order Landau energy density expansion for domain walls in AFE in the absence of stress and free electric field is written including the order parameters gradient terms:

$$\begin{aligned} \Delta Q &= \frac{1}{2} j\eta^2 + \frac{1}{4} k\eta^4 + \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 \\ &+ \frac{1}{2}\gamma P^2 \eta^2 + \frac{1}{2}\lambda \left(\frac{\partial \eta}{\partial x}\right)^2 + \frac{1}{2}\chi \left(\frac{\partial P}{\partial x}\right)^2 \end{aligned} \tag{21}$$

Where $\alpha = \alpha_0 (T - T_{CW})$ and $j = j_0 (T - T_{Cn})$ with T_{CW} and T_{Cn} representing the Curie-Weiss temperature and actual transition temperature, respectively. It was reported that for some groups of AFE perovskites, the T_{CW} values are lower than T_{Cn} values [22]. Rearrangement of equation 21 results to:

$$\begin{aligned} \Delta Q &= \frac{1}{2} j\eta^2 + \frac{1}{4} k\eta^4 + \frac{1}{2}(\alpha + \gamma\eta^2) P^2 \\ &+ \frac{1}{4}\beta P^4 + \frac{1}{2}\lambda \left(\frac{\partial \eta}{\partial x}\right)^2 + \frac{1}{2}\chi \left(\frac{\partial P}{\partial x}\right)^2 \end{aligned} \tag{22}$$

Now taking P and η as different order parameters and since AFE materials are centrosymmetric and therefore non-FE, into equation 22 one sets $P = 0$ and obtains:

$$\Delta Q = \frac{1}{2} j\eta^2 + \frac{1}{4} k\eta^4 + \frac{1}{2}\lambda \left(\frac{\partial \eta}{\partial x}\right)^2 \tag{23}$$

The equilibrium conditions of equation 23 for the function ΔQ of order parameter η can be obtained from the well-known Euler-Lagrange equation and results to:

$$\frac{\partial(\Delta Q)}{\partial \eta} - \frac{d}{dx}\left(\frac{\partial(\Delta Q)}{\partial \eta'}\right) = 0 \tag{24a}$$

$$\frac{\partial(\Delta Q)}{\partial \eta} = j\eta + k\eta^3 \tag{24b}$$

$$\frac{\partial(\Delta Q)}{\partial\eta'} = \lambda\frac{d}{dx}\eta' = \lambda\frac{d^2\eta}{dx^2} \quad (24c)$$

Adding the equations 24a, 24b and 24c together results to the second-order differential equation with a tanh kink-type solution [23] expressed as:

$$j\eta + k\eta^3 + \lambda\frac{d^2\eta}{dx^2} = 0 \quad (25)$$

$$\eta(x) = \eta_0 \tanh\left(\frac{x}{\sqrt{2\lambda/-j}}\right) = \eta_0 \tanh\left(\frac{x}{\xi}\right) \quad (26)$$

Where $\xi = \sqrt{-2\lambda/j}$ is the half-thickness of the AFE domain wall. Normalization of equation 26 gives $\eta(x)/\eta_0 = tanh(x/\xi)$ whose spatial numerical solution of order parameter profile appears to be as presented in the Figure 1.

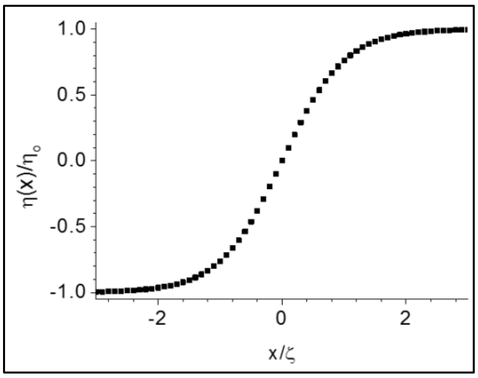

Fig. 1: AFE Domain Wall Spatial Profile for the Normalized Order Parameter $\eta(x)$.

3.1. Possibility of FE inside AFE walls

It is observed from the wall profile of Figure 1 that in the middle of the AFE domain wall the order parameter $\eta(x)$ equals zero. This disappearance of order parameter provides scope for assessing the possibilities of FE inside the wall. Thus, the observation that at the centre of the domain wall the order parameter $\eta(x)$ is equal to zero implies that in the middle of the wall the AFE structure is equal or at least very close to the high temperature parent phase. This gives the opportunity for inspecting FE in the wall. To begin with, one rewrites the AFE domain wall energy density of equation 21 replacing α and j with $\alpha_0(T - T_{CW})$ and $j_0(T - T_{Cn})$, respectively.

$$\Delta Q = \frac{1}{2}j_0(T - T_{C\eta})\eta^2 + \frac{1}{4}k\eta^4 + \frac{1}{2}(\alpha_0(T - T_{CW}) + \gamma\eta^2)P^2 + \frac{1}{4}\beta P^4 + \frac{1}{2}\lambda\left(\frac{\partial\eta}{\partial x}\right)^2 + \frac{1}{2}\chi\left(\frac{\partial P}{\partial x}\right)^2 \quad (27)$$

In equation 27 one can assume arbitrarily that:

i). $P = P_I$ gives the measure of FE and
ii). $\eta = P_{II}$ as measure of AFE

And so at the middle of the wall one inserts $\eta = 0$ into 27 to obtain:

$$\Delta Q(P, T, x) = \frac{1}{2}\alpha_0(T - T_{CW})P^2 + \frac{1}{4}\beta P^4 + \frac{1}{2}\chi\left(\frac{\partial P}{\partial x}\right)^2 \quad (28)$$

From the resulting changes of wall energy density at middle of the wall shown by expression 28, it is clear that for temperatures well below the Curie-Weiss temperature (T_{CW}), the stiffness coefficient, $\alpha = \alpha_0(T - T_{CW})$, becomes negative. This implies that FE may usually appear inside the AFE domain walls. However, if this happens, it is observed also that it will occur at some costs of instability penalties from the extra domain wall energy as a result of polarization energy gradient contributions to the total free energy of the system.

3.2. AFE domain walls polarization model

The observation that at the middle of the wall $\eta = 0$ constitutes an important criterion for proving the appearance of FE inside an AFE domain wall. However, the order parameter is not zero everywhere inside the wall. This means that polarization is not homogeneous throughout the wall and raises problems regarding polarization and energy gradient estimations. In Figure 2 an AFE domain wall and its numerical polarization model has been derived. With such a polarization pattern the maximum polarization is observed at the middle of the wall and decreases with spatial domain wall correlation length falling back to zero as the order parameter returns to its bulk absolute values. The AFE domain wall polarization model can be used to evaluate the observed FE inhomogeneities in AFE materials. Thus in the very proximity of the wall center, the change in wall correlation length is very small and the polarization attain its maximum value. However, far-away from the wall center the AFE domain wall energy density can be rewritten in a form that involves the averages of order parameter and polarization gradient terms. This is written as:

$$\Delta Q = \frac{1}{2}\alpha_0(T - T_{CW})P^2 + \frac{1}{2}\gamma P^2\bar{\eta}_0^2 + \frac{1}{4}\beta P^4 + \frac{1}{2}\chi\left(\frac{\partial\bar{P}}{\partial x}\right)^2 \quad (29)$$

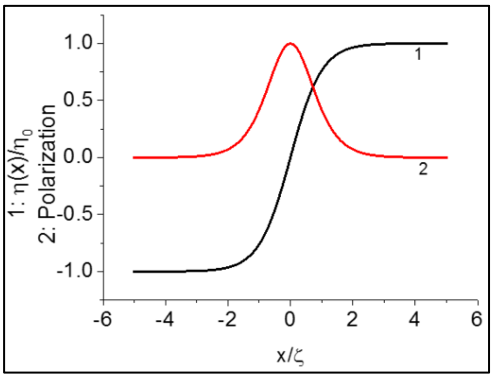

Fig. 2: AFE Domain Wall Model for Normalized 1: Order Parameter Profile and 2: Polarization Profile Inside the Wall.

Re-investigation of the order parameter profile and the polarization model in Figure 2, one can estimate that the average order parameter and average polarization gradient be deduced from:

$$\bar{\eta}_0 = \frac{\eta_0}{2} \quad (30a)$$

$$\frac{\partial\bar{P}}{\partial x} = \frac{P}{\xi} \quad (30b)$$

Inserting equation 31 into 30 results to:

$$\Delta Q = \frac{1}{2}\alpha_0(T - T_{CW})P^2 + \frac{1}{8}\gamma\eta_0^2P^2 + \frac{1}{4}\beta P^4 + \frac{1}{2}\chi\left(\frac{P}{\xi}\right)^2 \quad (31)$$

The value of order parameter, η_0 is obtained at equilibrium conditions when $\partial(\Delta Q)/\partial\eta = 0$, it is given by

$$\eta_0^2 = -j/k \quad (32)$$

The value of wall correlation length is equivalent to half the thickness of the domain wall:

$$\xi^2 = -2\lambda/j \quad (33)$$

Inserting equations 32 and 33 into 31 results to:

$$\Delta Q = \frac{1}{2}\alpha_0 (T - T_{CW})P^2 + \frac{1}{4}\beta P^4 + \frac{1}{8}\gamma\left(\frac{-j}{k}\right)P^2 + \frac{1}{4}\chi\left(\frac{-j}{\lambda}\right)P^2 \tag{34}$$

Energy density minimization with respect to P leads to:

$$\frac{\partial(\Delta Q)}{\partial P} = \alpha_0 (T - T_{CW})P + \frac{1}{4}\gamma\left(\frac{-j}{k}\right)P + \frac{1}{2}\chi\left(\frac{-j}{\lambda}\right)P + \beta P^3 = 0 \tag{35}$$

$$\frac{\partial(\Delta Q)}{\partial P} = \left[\alpha_0 (T - T_{CW}) + \frac{1}{4}\left(\chi\left(\frac{-j}{\lambda}\right) + 2\gamma\left(\frac{-j}{k}\right)\right)\right]P + \beta P^3 = 0 \tag{36}$$

$$P^2 = \frac{\left[\alpha_0 (T - T_{CW}) + \frac{1}{4}(-j)\left(\frac{\chi}{\lambda} + \frac{2\gamma}{k}\right)\right]}{-\beta} \tag{37}$$

Using $j = j_0(T - T_{Cn})$,

$$P^2 = \frac{\left[\alpha_0 (T_{CW} - T) + \frac{1}{4} j_0\left((T - T_{C\eta})\left(\frac{\chi}{\lambda} + \frac{2\gamma}{k}\right)\right)\right]}{\beta} \tag{38}$$

One can see from this analytical model that if the coefficients which appear in equation 38 are known, at high and low temperatures, this would behave according to the Curie-Weiss law. This gives signs for appearance of FE or stable polarization states inside AFE domain walls and suggest that probably the critical temperature points at which FE appears in given AFE materials can be theoretically derived. So then, the phase transition temperature, T_0^* is obtained when $P^2(T = T_0^*) = 0$. This is given by:

$$T_0^* = \frac{\alpha_0 T_{CW} - \frac{1}{4} j_0 T_{C\eta}\left(\frac{\chi}{\lambda} + \frac{2\gamma}{k}\right)}{\alpha_0 - \frac{1}{4} j_0\left(\frac{\chi}{\lambda} + \frac{2\gamma}{k}\right)} \tag{39}$$

Or equivalently as,

$$T_0^* = T_{CW}\left[\frac{\alpha_0 - \frac{1}{4} j_0 \frac{T_{C\eta}}{T_{CW}}\left(\frac{\chi}{\lambda} + \frac{2\gamma}{k}\right)}{\alpha_0 - \frac{1}{4} j_0\left(\frac{\chi}{\lambda} + \frac{2\gamma}{k}\right)}\right] \tag{40}$$

4. Conclusion

Landau-Kittel theory has been successfully used to study the phenomenological behaviours of antiferroelectric ferroics with accent on phase transitions that can result to ferroelectric properties. Accordingly, the spatial distribution of the order parameter inside an antiferroelectric domain wall was derived and tested for possibilities of having ferroelectricity inside it. It was proved that ferroelectricity can appear inside the wall but with evidences of increasing system instability because of the polarization gradient term that results to additional energy in the system.

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