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Thermodynamic properties of temperature graded ferroelectric film

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Abstract
Effects of quantum fluctuation and four-spin interaction on the polarization and pyroelectric coefficient of temperature graded ferroelectric film are investigated, based on the transverse Ising model by taking into account the four-spin interaction. It is found that the magnitude and the sign of the polarization gradient are dependent on the imposed temperature gradient, and both the quantum fluctuation and four-spin interaction play an important role in the thermodynamic properties of the temperature graded film. With increasing strength of the quantum fluctuations the sharp peak of the pyroelectric coefficient shifts to lower temperatures. Also the four-spin interaction increases the mean polarization and makes the smooth pyroelectric peak at low temperature more pronounced. Furthermore, the graded ferroelectric film shows the characteristic feature of a first-order phase transition when the four-spin interaction is larger than a critical value, which is dependent on the temperature gradient and the quantum fluctuation.

1. Introduction

With the rapid development of advanced synthesis techniques, much attention has been focused on the study of functionally graded ferroelectrics because they exhibit some new behaviour and properties that have not been observed in homogeneous bulk or thin film ferroelectrics [1–4]. Functionally graded ferroelectrics are characterized by their polarization gradients normal to the growth surface of thin film structures, or equivalently in bulk materials by their polarization gradients along the electric field line connecting the surfaces of the electrodes when configured as capacitors. Many experiments show that one of the most notable properties of these functionally graded ferroelectrics is the offset in hysteresis loop along the polarization axis when excited with an alternating electric field. In addition, the position and direction of the offsets observed experimentally are found to be determined by the polarization gradient, the

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temperature, the strain and the magnitude of the periodic excitation field—'the pumping force'. The shifted hysteresis loops are attributed to 'built-in' potentials, analogous to the asymmetric current–voltage characteristics resulting from the 'built-in' potential across chemically doped regions in semiconductor diode junctions. Therefore, the graded structures have given rise to a particular class of transcapacitive ferroelectric devices [5], having potential applications in infared detection and actuation, as well as tunable microwave devices, such as filters and phase shifters [6, 7].

It is well known that the ferroelectric spontaneous polarization is a function of material composition, temperature and stress [8]. Consequently, it has been possible to form graded-ferroelectric devices from a variety of material systems, both by grading the composition of the ferroelectrics and by imposing a temperature gradient normal to the electrode surfaces. Such materials have displayed new properties and provided a rich area for experimental and theoretical research. Giant effective pyroelectric coefficients were obtained from compositionally graded barium strontium titanate ferroelectric thin film devices formed on silicon substrate using unbalanced magnetron sputter deposition [9]. 'Up' and 'down' hysteresis offsets were experimentally observed when temperature gradients were imposed across a bulk ferroelectric material [10]. Theoretically, a Landau–Ginzburg thermodynamic model was constructed and used to develop a methodology for analysing temperature graded ferroelectrics [11]. The polarization gradients resulted in asymmetric hysteresis with 'up' and 'down' charge offsets.

In the theoretical treatment, there are two approaches used to study ferroelectric behaviour: Ginzburg–Landau–Devonshire (GLD) phenomenological theory and the microscopic transverse Ising model (TIM) [12]. The well known TIM has been successfully applied to study the properties of homogeneous finite-size ferroelectrics, such as ferroelectric superlattice, film and bilayer structures. As we know, the GLD theory is a macroscopic theory, thus the quantum effect cannot be taken into consideration. On the other hand, quantum fluctuation typically has a very important effect on the structural and thermodynamic properties of materials consisting of light atoms such as hydrogen and helium, and the cubic perovskites, which can exhibit a decisive quantum fluctuation effect despite the fact that the lightest constituent is oxygen. This can occur because these materials have several competing structures with very small structural and energetic differences. Zhong and Vanderbilt [13] have studied the effects of quantum fluctuation on structural phase transitions in $SrTiO_3$ and $BaTiO_3$. For $BaTiO_3$, they found that the quantum fluctuation reduced the transition temperature by 35–50 K. Although Wang *et al* [14] analysed the phase transition properties of temperature graded ferroelectric films by use of TIM, the tunnelling frequency was independent of the temperature of each layer, as well as four-spin interaction being neglected. Since many ferroelectric materials undergo first-order phase transitions, it is practical and interesting to study their thermodynamic properties. In order to study first-order phase transitions, a four-spin exchange interaction term $J'_{ijkl}S_i^zS_j^zS_k^zS_l^z$ must be introduced into the Hamiltonian of TIM [15], which is analogous to a negative four-order polarization coefficient in GLD theory and thus yields a first-order transition above a critical threshold. The main purpose of the present paper is to systematically investigate the impacts of quantum fluctuation and four-spin interaction on the thermodynamic properties of temperature graded ferroelectric film, described by the TIM, by taking into account the four-spin interaction.

2. Model and formulation

We consider a monodomain $BaTiO_3$ ferroelectric film with N layers, sandwiched between two metallic electrodes, as illustrated in figure 1. Each layer is defined on the x–y plane

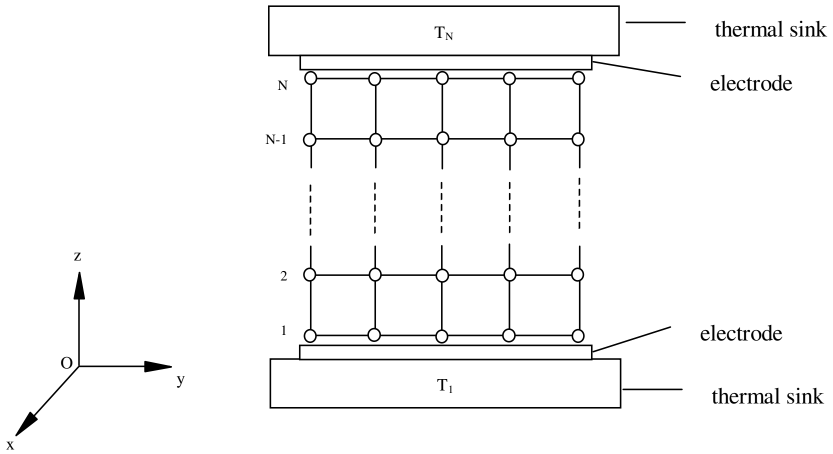

Figure 1. Schematic representation of the model of temperature graded $BaTiO_3$ ferroelectric film. The z direction is perpendicular to the film surface.

and the pseudo-spin's site on a square lattice. The two electrodes are in contact with thermal sinks at temperatures T_1 and T_N, imposing a temperature gradient across the ferroelectric film. Considering the four-spin interaction, the Hamiltonian of the system is described by TIM as

$$H = -\sum_{\langle ij\rangle} J_{ij} S_i^z S_j^z - \sum_{\langle ijkl\rangle} J'_{ijkl} S_i^z S_j^z S_k^z S_l^z - \sum_i \Omega_i S_i^x - 2\mu E \sum_i S_i^z, \tag{1}$$

where S_i^x and S_i^z are the x- and z-components of the spin-1/2 operator at site i, J_{ij} is the coupling coefficient between the nearest neighbour sites i and j, J'_{ijkl} is the four-spin interaction coefficient, Ω_i is the tunnelling frequency, μ is the effective dipole moment on site i, and E is the applied electric field. We assume that the z direction is perpendicular to the film surface and the polarization is along the z direction. Within the framework of the mean field approximation, assuming that the pseudo-spins have the same value in the same layer, the average spin along the z direction in the ith layer can be expressed as follows:

$$R_i = \langle S_i^z\rangle = \frac{\langle H_i^z\rangle}{2|H_i|}\tanh\frac{|H_i|}{2k_B T_i}, \tag{2}$$

where

$$H_i = \left(\Omega_i, 0, \sum_j J_{ij}\langle S_j^z\rangle + \sum_{jkl} J'_{ijkl}\langle S_j^z\rangle\langle S_k^z\rangle\langle S_l^z\rangle + 2\mu E\right)$$

is the mean field acting on the ith layer pseudo-spin. As the four-spin interactions are between four spins either in the same layer or in the two neighbouring layers, the interaction coefficient J'_{ijkl} can be simplified as J'_{ij}; then we have

$$\langle H_i^z\rangle = J_{i,i-1}R_{i-1} + 4J_{i,i}R_i + J_{i,i+1}R_{i+1} + 4J'_{i,i-1}R_iR_{i-1}^2 + 4J'_{i,i+1}R_iR_{i+1}^2 + 4J'_{i,i}R_i^3 + 2\mu E, \tag{3}$$

$$|H_i| = \sqrt{\Omega_i^2 + (\langle H_i^z\rangle)^2}, \tag{4}$$

$$T_i = T_1 + (i-1)\Delta T. \tag{5}$$

T_i is the temperature of the ith layer, and ΔT is the temperature increment per layer which scales the magnitude of the temperature gradient. i runs over all the layers in the ferroelectric film.

In order to take into account the quantum fluctuation, we suppose [15]

$$\Omega_i = g\Omega_{T0}\left(1 - \frac{T_i}{391}\right) + \Omega_{T0}, \tag{6}$$

where g is a parameter which indicates the strength of quantum fluctuation and Ω_{T0} is the tunnelling frequency at the actual Curie–Weiss temperature T_0 (391 K) for $BaTiO_3$ ferroelectric film. To date, no one has investigated the effect of quantum fluctuation on the thermodynamic properties of temperature graded ferroelectric film. Equation (6) shows that the tunnelling frequency is dependent on the temperature of the specific layer and has different values for each layer because of the existence of the temperature gradient in the film. Zhong and Vanderbilt [13] have proved that the quantum fluctuations will increase with decreasing temperature. This suggests that the tunnelling frequency will, on average, increase with decreasing temperature. According to equation (6), the tunnelling frequency Ω_i of the ith layer will increase linearly from Ω_{T0} to $(g + 1)\Omega_{T0}$ when the temperature decreases from 391 to 0 K. Therefore, the $k_B T_i$ in equation (2) represents the contribution of the thermal fluctuation, and the tunnelling frequency Ω_i represents the contribution of the quantum fluctuation. Zhang *et al* [15] have given a qualitative analysis for equation (6). For $BaTiO_3$, an eight-site potential exists around the Ti ion. The height h of the potential barrier is finite. When $k_B T_i$ is higher than the height h, the tunnelling effect does not exist. This means $\Omega_i = 0$. For low temperature, $k_B T_i$ will be lower than the height h, thus the tunnelling effect will exist. We then obtain $\Omega_i > 0$.

Let $\alpha_i = 2|H_i|/\tanh(|H_i|/2k_B T_i)$, then R_i satisfies the following equation without applied electric field according to equations (2) and (3):

$$4J'_{i,i}R_i^3 + [(4J_{i,i} - \alpha_i) + 4J'_{i,i-1}R_{i-1}^2 + 4J'_{i,i+1}R_{i+1}^2]R_i + J_{i,i-1}R_{i-1} + J_{i,i+1}R_{i+1} = 0. \tag{7}$$

The above equation stands for a set of nonlinear simultaneous equations from which R_i can be calculated numerically. Then the average polarization of the ferroelectric film can be obtained:

$$\langle P\rangle = \frac{1}{N}\sum_{i=1}^{N} 2n\mu R_i, \tag{8}$$

where n is the number of pseudo-spins in a unit volume.

The mean pyroelectric coefficient of the film can be expressed by

$$p = \frac{1}{N}\sum_{i=1}^{N}\frac{\partial P_i}{\partial T_i} = \frac{1}{N}\sum_{i=1}^{N} 2n\mu\frac{\partial R_i}{\partial T_i}. \tag{9}$$

$\partial R_i/\partial T_i$ satisfies the following equation:

$$\frac{\partial R_i}{\partial T_i} = \frac{\Omega_i^2 K_i - \Omega_i\langle H_i^z\rangle(-g\Omega_{T0}/391)}{|H_i|^2\alpha_i} + \left[1 - \tanh^2\left(\frac{|H_i|}{2k_B T_i}\right)\right] \times \frac{\Omega_i T_i\langle H_i^z\rangle(-g\Omega_{T0}/391) + T_i\langle H_i^z\rangle^2 K_i - |H_i|^2\langle H_i^z\rangle}{4k_B T_i^2|H_i|^2}, \tag{10}$$

where

$$K_i = \frac{\partial\langle H_i^z\rangle}{\partial T_i} = [12J'_{i,i}R_i^2 + 4J_{i,i} + (4J'_{i,i-1}R_{i-1}^2 + 4J'_{i,i+1}R_{i+1}^2)]\frac{\partial R_i}{\partial T_i} + \left(8J'_{i,i-1}R_{i-1}\frac{\partial R_{i-1}}{\partial T_{i-1}} + 8J'_{i,i+1}R_{i+1}\frac{\partial R_{i+1}}{\partial T_{i+1}}\right)R_i + J_{i,i-1}\frac{\partial R_{i-1}}{\partial T_{i-1}} + J_{i,i+1}\frac{\partial R_{i+1}}{\partial T_{i+1}}. \tag{11}$$

Combining equation (10) with (7), $\partial R_i/\partial T_i$ can be calculated numerically.

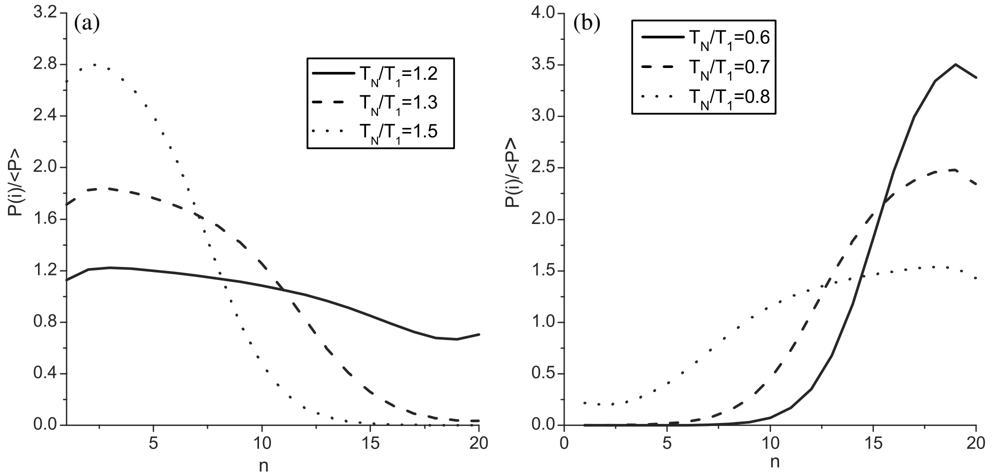

Figure 2. The normalized polarization with respect to average polarization as a function of position at the given quantum fluctuation parameter $g = 1.0$ and the four-spin interaction parameter $J' = 200.0\ k_B$, (a) and (b) corresponding to positive and negative temperature gradients, respectively.

3. Results and discussion

In our calculation, the total thickness of the ferroelectric film is fixed as $N = 20$, and the values of the parameters are chosen appropriate to $BaTiO_3$ ferroelectric film. We take the nearest-neighbouring interaction parameter $J = 277.8\ k_B$ and the tunnelling frequency $\Omega_{T0} = 384.4\ k_B$ [15]. Since the properties of the surface are different from those of the bulk, we distinguish the interactions of pseudo-spin and the tunnelling frequency on the surface and inside the film. The parameters of the film surface are taken for $J_S = 1.45J$, $J'_S = 1.45J'$, and $\Omega'_S = 1.45\ \Omega$.

To analyse the effect of temperature gradient on the polarization, T_1 is fixed at 328 K if $T_N > T_1$, or T_N is fixed at 328 K if $T_N < T_1$. We plot the normalized polarization with respect to average polarization $\langle P \rangle$ as a function of position for three different temperature gradients in figures 2(a) and (b), given the quantum fluctuation parameter $g = 1.0$ and the four-spin interaction parameter $J' = 200.0\ k_B$ [16]. As can be seen from figure 2, a polarization gradient is demonstrated inside the film which obviously results from the temperature gradient, and the magnitude and the direction of the polarization gradient depend on the temperature gradient imposed on the ferroelectric film. Although the temperature gradient is uniform, the polarization gradient is not uniform for the given value of T_N/T_1. If there is a positive temperature gradient along the z direction (that is $T_N > T_1$) as seen in figure 2(a), a continuously declining polarization profile is obtained away from the surface. Furthermore, the polarization profile becomes steeper with increasing temperature gradient. It is interesting that all the layers in the film are in the ferroelectric phase for small temperature gradient ($T_N/T_1 = 1.2$, 1.3), but some layers remain in the ferroelectric phase while the others are already in the paraelectric phase for large temperature gradient ($T_N/T_1 = 1.5$). The larger the temperature gradient, the more layers are in the paraelectric phase. Figure 2(b) corresponds to the case in which a negative temperature gradient (that is $T_N < T_1$) is imposed on the ferroelectric film. In this case, the polarization profile is inverted in comparison to the positive temperature gradient. These results are qualitatively consistent with those using the Landau–Ginzburg thermodynamic model [11].

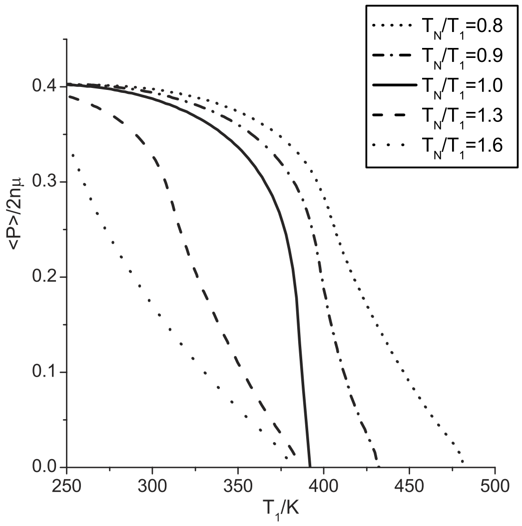

Figure 3. The mean polarization as a function of the temperature in the bottom layer T_1 for different temperature ratio values $T_N/T_1 = 0.8, 0.9, 1.0, 1.3, 1.6$, at selected quantum fluctuation parameter $g = 1.0$ and four-spin interaction parameter $J' = 200.0\ k_B$.

The mean polarization as a function of the temperature in the bottom layer T_1 is shown in figure 3 for different ratio values of T_N/T_1 ($T_N/T_1 = 0.8, 0.9, 1.0, 1.3, 1.6$) at the selected quantum fluctuation parameter $g = 1.0$ and the four-spin interaction parameter $J' = 200.0\ k_B$. It must be noted that the temperature gradient will increase with the increase of the ratio value of T_N/T_1 ($T_N > T_1$) or decrease with the increase of T_N/T_1 ($T_N < T_1$) for a given T_1. For the negative temperature gradient ($T_N/T_1 = 0.8, 0.9$), the mean polarization of the film increases with the increase of the temperature gradient at any given T_1. It is easy to understand that the ferroelectricity of each layer is dependent on the temperature. For a given temperature of bottom layer T_1, the larger the temperature gradient, the lower the temperature of the other layers in the film; therefore, the polarizations of these layers are larger. However, for the positive temperature gradient ($T_N/T_1 = 1.3, 1.6$), the opposite results can be obtained. Furthermore, we can see that the phase transition temperature is shifted to higher temperature for the negative temperature gradient. In contrast, the positive temperature gradient slightly lowers the phase transition temperature. That is, the influence of the negative temperature gradient on the phase transition temperature is more obvious than that of the positive temperature gradient. From figure 3, we also can see that the larger the temperature gradient, the more pronouncedly the polarization differs from that of the ferroelectric film without the temperature gradient ($T_N = T_1$).

Figure 4 exhibits the temperature in the bottom layer T_1 dependence of the mean polarization for different quantum fluctuation values g ($g = 0, 1.0, 1.5, 2.0$) at the given four-spin interaction parameter $J' = 200.0\ k_B$ and the temperature ratio value $T_N/T_1 = 1.3$. We find that the influence of quantum fluctuation is not apparent approaching the phase transition temperature [15]. From figure 4 we can easily understand that the quantum fluctuation effect will increase with decreasing temperature T_1 and low temperature gradient.

The effect of temperature gradient on the pyroelectric coefficient of the film is plotted in figure 5 for different temperature ratios T_N/T_1 ($T_N/T_1 = 0.9, 1.0$, and 1.3), at a selected quantum fluctuation parameter $g = 1.0$ and the four-spin interaction parameter $J' = 200.0\ k_B$.

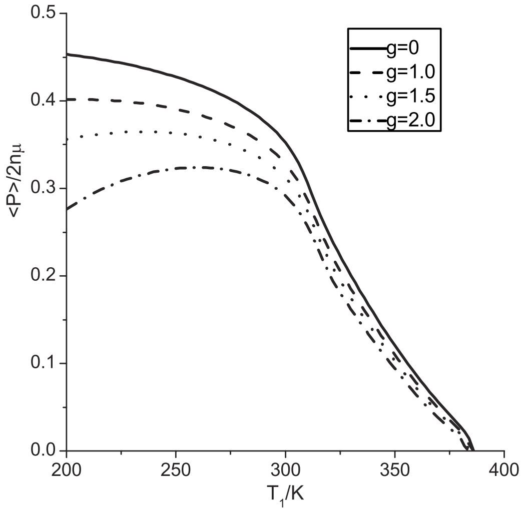

Figure 4. The temperature in the bottom layer T_1 dependence of the mean polarization for different quantum fluctuation parameters $g = 0, 1.0, 1.5, 2.0$, at selected $T_N/T_1 = 1.3$ and the four-spin interaction parameter $J' = 200.0\ k_B$.

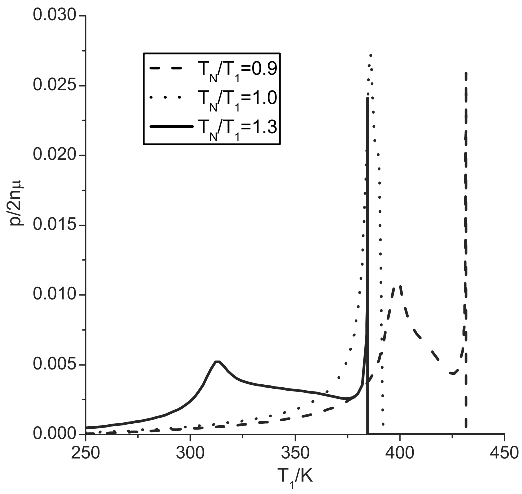

Figure 5. The temperature in the bottom layer T_1 dependence of the pyroelectric coefficient for different temperature ratio values $T_N/T_1 = 0.9$, 1.0, and 1.3, at given quantum fluctuation parameter $g = 1.0$ and the four-spin interaction parameter $J' = 200.0\ k_B$.

It can be seen that the pyroelectric coefficient shows the same feature as that of the bulk material while there is no temperature gradient ($T_N = T_1$), and only one sharp peak occurs at the phase transition temperature of the film. Irrespective of the positive temperature gradient and the negative temperature gradient, the broad and smooth peak occurs at a low temperature. This phenomenon may have potential applications in designing pyroelectric devices. Because of the temperature gradient, when some layers transfer to be disordered, the other layers are still in the ordered state, which will affect the polarization state of the whole thin film. Besides, the negative temperature gradient significantly results in a shift of the pyroelectric coefficient

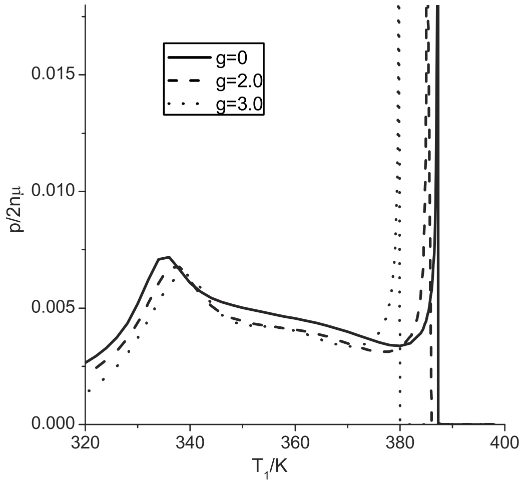

Figure 6. The temperature in the bottom layer T_1 dependence of the pyroelectric coefficient for different quantum fluctuation parameters $g = 0, 2.0$, and 3.0, at selected $T_N/T_1 = 1.2$ and the four-spin interaction parameter $J' = 200.0\,k_B$.

maximum towards higher temperature, which is consistent with the result of figure 3 that the negative temperature gradient obviously changes the phase transition temperature. It is also shown that there is a good qualitative agreement with the observed behaviour in temperature gradient deuterated triglycine sulfate (DTGS) films [17], that is the existence of positive temperature gradient results in a shift of the pyroelectric coefficient maximum towards lower temperature.

Figure 6 displays the temperature in the bottom layer T_1 dependence of the pyroelectric coefficient for selected quantum fluctuation parameters g ($g = 0, 2.0$, and 3.0), at the same temperature ratio value $T_N/T_1 = 1.2$ and the four-spin interaction parameter $J' = 200.0\,k_B$. The pyroelectric coefficient maximum varies its position with the variation of quantum fluctuation and the effect of quantum fluctuation on the pyroelectric peak is different in the low temperature and high temperature regions. The temperature corresponding to the sharp peak of the pyroelectric coefficient shifts to lower temperature with the increase of the quantum fluctuation parameter. However, the broad and round pyroelectric peak maximum shifts to higher temperature with the increase of the quantum fluctuation parameter.

To better understand the impact of four-spin interaction on the thermodynamic properties of ferroelectric film, variations of the mean polarization as a function of temperature in the bottom layer T_1 for different interaction parameters J' ($J' = 0, 200.0\,k_B, 300.0\,k_B, 400.0\,k_B$, and $450.0\,k_B$) are depicted in figure 7. The quantum fluctuation parameter and the temperature ratio value are fixed as $g = 1.0$ and $T_N/T_1 = 1.3$, respectively. It is easy to see that the four-spin interaction increases the mean polarization of the film for a given temperature in the lowest layer, but it has little influence upon the transition temperature. Moreover, the four-spin interaction makes the variation of polarization with the temperature more abrupt close to the transition temperature. With the increase of four-spin interaction parameter, the strength of spin–spin exchange interaction increases, which contributes to the polarization. It is interesting that we can find a critical value of four-spin interaction parameter $J'_C = 366.0\,k_B$, which exhibits a crossover from second-order phase transition to first-order phase transition. When $J' > J'_C$, the graded ferroelectric film shows the characteristic feature of first-order phase transition. When the four-spin interaction parameter is larger than the critical value,

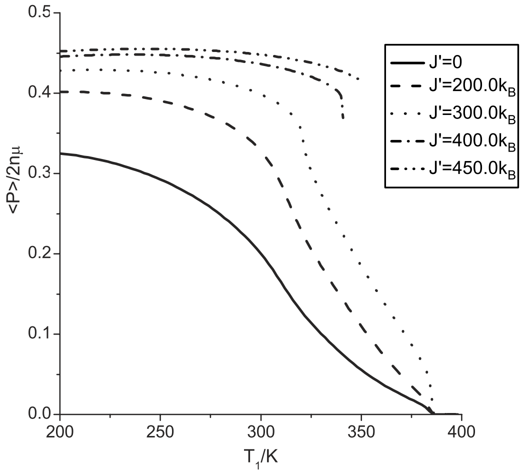

Figure 7. Variations of the mean polarization as a function of the temperature in the bottom layer T_1 for different four-spin interaction parameters $J' = 0, 200\ k_B, 300\ k_B, 400\ k_B$, and $450\ k_B$, at fixed positive temperature ratio value $T_N/T_1 = 1.3$, $g = 1.0$.

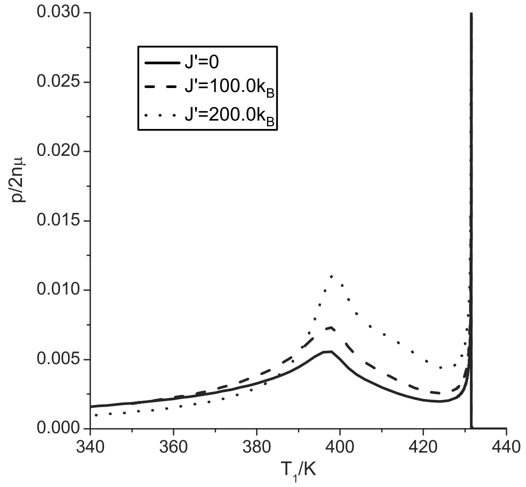

Figure 8. Variations of the pyroelectric coefficient as a function of the temperature in the bottom layer T_1 for different four-spin interaction parameters $J' = 0$, $100.0\ k_B$, and $200.0\ k_B$, at fixed negative temperature ratio value $T_N/T_1 = 0.9$, $g = 1.0$.

the first-order phase transition firstly occurs in some layers with higher temperature due to the temperature gradient. Besides, the theoretical computation results reveal that the value of the critical four-spin interaction is mainly dependent on the temperature gradient and quantum fluctuation. The critical value of four-spin interaction parameter decreases with the increase of quantum fluctuation, but increases with the increase of temperature gradient.

Figure 8 shows variations of the pyroelectric coefficient as a function of temperature in the bottom layer T_1 for different four-spin interaction parameters J' ($J' = 0, 100.0\ k_B$, and $200.0\ k_B$), at selected quantum fluctuation parameter $g = 1.0$, $T_N/T_1 = 0.9$. From figure 8 we can conclude that the four-spin interaction makes the smooth pyroelectric peak at low temperature more pronounced and slightly shift to high temperature, but it does not affect the position of the sharp pyroelectric peak, which is in agreement with the result of figure 7. That is, the four-spin interaction does not change the transition temperature when $J' < J'_C$.

4. Conclusion

In summary, effects of quantum fluctuation and temperature gradient on the spontaneous polarization and the pyroelectric coefficient of a temperature graded $BaTiO_3$ ferroelectric film have been theoretically investigated, based on the TIM by taking into account the four-spin interaction. The calculated results demonstrate that the magnitude and the sign of the polarization gradient are dependent on the imposed temperature gradient, as well as both the quantum fluctuation and four-spin interaction playing an important role in the thermodynamic properties of the temperature graded film. We find that the influence of quantum fluctuation will increase with decreasing temperature, and the four-spin interaction not only increases the mean polarization but also makes the smooth pyroelectric peak at low temperature sharper. Furthermore, we find a critical value of four-spin interaction parameter for a given temperature gradient, and the graded ferroelectric film exhibits first-order phase transition when the four-spin interaction parameter is larger than this critical value, which is related to the quantum fluctuation and the temperature gradient.

Acknowledgments

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