Effects of multi-surface modification on Curie temperature of ferroelectric films

Effects of multi-surface modification on Curie temperature of ferroelectric films

Xiao-Guang Wang†, Shao-Hua Pan‡ and Guo-Zhen Yang‡

† Laboratory of Optical Physics, Institute of Physics, Chinese Academy of Sciences,
Beijing 100080, People's Republic of China
‡ China Center of Advanced Science and Technology (World Laboratory), PO Box 8730,
Beijing 100080, People's Republic of China and Institute of Physics,
Chinese Academy of Sciences, Beijing 100080, People's Republic of China

E-mail: `xyw@aphy.iphy.ac.cn`

Abstract. Within the framework of mean field theory, we study the effects of multi-surface modification on the Curie temperature of ferroelectric films using the transverse Ising model. The general nonlinear equations for Curie temperature of multi-surface ferroelectric films with arbitrary exchange constants and transverse fields are derived by the transfer matrix method. As an example, we consider an (l, n, l) film consisting of l top surface layers, n bulk layers and l bottom surface layers. Two types of surface modification, modifications of a surface exchange constant and a surface transverse field, are taken into account. The dependence of Curie temperature on the surface layer numbers, bulk layer numbers, surface exchange constants, surface transverse fields and bulk transverse fields is discussed.

1. Introduction

Size effects are expected to be particularly important in materials that undergo phase transitions, such as ferromagnets, superconductors and ferroelectrics [1–3]. In recent years, there has been considerable interest in the effects of size and surface on the ferroelectric phase transition due to the developments of ferroelectric films and composite materials [4–20]. Nonvolatile memories and other applications have made ferroelectric films a subject of great practical importance [21].

An early study on KDP fine particles embedded in an insulating medium showed no ferroelectric phase transition if their size is less than 150 nm [22], while Anliker *et al* demonstrated that the transition temperature of $BaTiO_3$ increases as the particle size decreases [23]. Controversial results obtained from $BaTiO_3$ [24] fine particles and $PbTiO_3$ fine particles [25] show that the transition temperature decreases with decrease in grain size.

Theoretically, much work has been done on the Laudau phenomenological theory of phase transition in ferroelectric films [6, 8, 10, 11]. On the microscopic level, the pseudo-spin theory based on the transverse Ising model (TIM) was first introduced by de Gennes [26] to describe the phase transition of hydrogen-bonded ferroelectrics. The model has been applied to many other systems such as ferromagnetic systems [27] and Jahn–Teller systems [28]. The surface exchange constant and surface layer thickness dependence of the Curie temperature of ultra-thin ferroelectric films is studied numerically by considering two types of surface modification of the exchange constants [29]. The Curie temperature for ferroelectric films of arbitrary thickness has been considered and modification of both surface exchange constants

and surface transverse field is included [30, 31]. The effects of few surface layers ($l = 1, 2$) of ferroelectric (l, n, l) films on Curie temperature have been studied in previous works. Little theoretical work has been devoted to the effects of multi-surface modification ($l \geqslant 3$) on the Curie temperature. In practice, there exist multiple surface layers in ferroelectric films fabricated by present experimental techniques.

In this article, we study the ferroelectric (l, n, l) films of arbitrary surface layers l and bulk layers n and take into account two types of surface modification, modification of surface exchange constant J_s and surface transverse field Ω_s. By using the transfer matrix method introduced for ferromagnetic superlattices [32], an explicit and general nonlinear equation for the Curie temperature is obtained. We give the equation in the following section. The dependences of Curie temperature on surface layer numbers, bulk layer numbers, surface exchange constants and surface transverse fields are discussed in section 3 and the conclusion is given in the last section.

2. Transverse Ising model and transfer matrix method

We start with the TIM [26, 29, 30]

$$H = -\frac{1}{2} \sum_{(i,j)} \sum_{(r,r')} J_{ij} S_{ir}^z S_{jr'}^z - \sum_{ir} \Omega_i S_{ir}^x \tag{1}$$

where S_{ir}^x and S_{ir}^z are the x and z components of the pseudo-spin, (i, j) are plane indices and (r, r') are different sites of the planes, J_{ij} denote the exchange constants. We assume that the transverse field Ω_i is dependent only on layer index and consider the interaction between neighbouring sites.

The spin average $\langle \vec{S}_i \rangle$ is obtained from the mean field theory [29, 30]

$$\langle \vec{S}_i \rangle = \frac{\vec{H}_i}{2|\vec{H}_i|} \tanh(|\vec{H}_i|/2k_B T) \tag{2}$$

where $\vec{H}_i(\Omega_i, 0, \sum_j J_{ij} \langle S_j^z \rangle)$ is the mean field acting on the ith spin, k_B is the Boltzmann constant and T is the temperature.

At temperature close to and below the Curie temperature, $\langle S_i^x \rangle$ and $\langle S_j^z \rangle$ are small, $|\vec{H}_i| \approx \Omega_i$, equation (2) can be approximated as

$$\langle S_i^x \rangle = (1/2) \tanh(\Omega_i/2k_B T) \tag{3}$$

$$\langle S_i^z \rangle = \lfloor z_0 J_{ii} \langle S_i^z \rangle + z(J_{i,i+1} \langle S_{i+1}^z \rangle + J_{i,i-1} \langle S_{i-1}^z \rangle) \rfloor (1/2\Omega_i) \tanh(\Omega_i/2k_B T). \tag{4}$$

Here z_0 and z are the numbers of nearest neighbours in a certain plane and between successive planes respectively. By defining

$$K_i = z_0 J_{ii}/zJ \qquad K_{i,i+1} = J_{i,i+1}/J \qquad K_{i,i-1} = J_{i,i-1}/J \qquad m_i = \langle S_i^z \rangle$$
$$\tau_i = (2\Omega_i/zJ) \coth(\Omega_i/2k_B T), \tag{5}$$

equation (4) can be written as

$$(\tau_i - K_i)m_i - K_{i,i+1}m_{i+1} - K_{i,i-1}m_{i-1} = 0. \tag{6}$$

Here J is the interlayer exchange constant in the bulk.

Let us rewrite the above equation in matrix form in analogy with [32]

$$\begin{pmatrix} m_{i+1} \\ m_i \end{pmatrix} = M_i \begin{pmatrix} m_i \\ m_{i-1} \end{pmatrix} \tag{7}$$

with M_i as the transfer matrix defined by

$$M_i = \begin{pmatrix} (\tau_i - K_i)/K_{i,i+1} & -K_{i,i-1}/K_{i,i+1} \\ 1 & 0 \end{pmatrix}. \tag{8}$$

We assume that the ferroelectric film contains $N + 1$ layers with layer indices $i = 0, 1, 2, \ldots, N$. From equation (7), we obtain

$$\begin{pmatrix} m_N \\ m_{N-1} \end{pmatrix} = R \begin{pmatrix} m_1 \\ m_0 \end{pmatrix} \tag{9}$$

where $R = M_{N-1} \ldots M_2 M_1$ represents successive multiplication of the transfer matrices.

For an ideal film system, there exists symmetry in the direction perpendicular to the surface, which allows us to write $m_i = m_{N-i}$. Then, the following nonlinear equations for Curie temperature can be obtained from equations (6) and (9) as

$$R_{11}[(\tau_0 - K_0)/K_{0,1}]^2 + (R_{12} - R_{21})[(\tau_0 - K_0)/K_{0,1}] - R_{22} = 0. \tag{10}$$

The above equation is the general equation for Curie temperature for arbitrary exchange constants J_{ij} and transverse field Ω_i.

For a uniform system of $N + 1$ layers with $J_{ij} = J$ and $\Omega_i = \Omega$, equation (10) reduces to

$$R_{11}(\tau - z_0/z)^2 + (R_{12} - R_{21})(\tau - z_0/z) - R_{22} = 0 \tag{11}$$

where $\tau = (2\Omega/zJ) \coth(\Omega/2k_B T)$. The total transfer matrix

$$R = \begin{pmatrix} \tau - z_0/z & -1 \\ 1 & 0 \end{pmatrix}^{N-1}. \tag{12}$$

The Nth power of a unimodular 2×2 matrix A can be simplified as [33]

$$A^N = U_N A - U_{N-1} I \tag{13}$$

where I is the 2×2 unit matrix and $U_N = (\lambda_+^N - \lambda_-^N)/(\lambda_+ - \lambda_-)$. λ_+ and λ_- are the two eigenvalues of the matrix A.

From equations (12) and (13), we obtain the matrix elements of R as follows

$$R_{11} = (\tau - z_0/z)U_{N-1} - U_{N-2}$$
$$R_{12} = -U_{N-1} \qquad R_{21} = U_{N-1}$$
$$R_{22} = -U_{N-2}. \tag{14}$$

Here, $\lambda_\pm = [\tau - z_0/z \pm \sqrt{(\tau - z_0/z)^2 - 4}]/2$. From the definition of U_N and relations $\lambda_+ + \lambda_- = \tau - z_0/z$ and $\lambda_+ \lambda_- = 1$, we have the recursion relations

$$U_N = (\lambda_+ + \lambda_-)U_{N-1} - U_{N-2} \tag{15}$$
$$U_{N+2} = (\lambda_+ + \lambda_-)^2 U_N - 2(\lambda_+ + \lambda_-)U_{N-1} + U_{N-2}. \tag{16}$$

Substituting equation (14) into equation (11) and using the above relations, we reduce equation (11) to its simplest form

$$U_{N+2} = 0 \tag{17}$$

which is identical with the result of [30].

U_{N+2} can be written as

$$U_{N+2} = \sin[(N + 2)\phi]/\sin \phi \tag{18}$$

for $(\tau - z_0/z)^2 \leqslant 4$. Here $\phi = \arccos[(\tau - z_0/z)/2]$. For $(\tau - z_0/z)^2 \geqslant 4$, ϕ becomes $i\theta$, and the trigonometric functions become hyperbolic functions of θ.

Equation (17) gives

$$(2\Omega/zJ) \coth(\Omega/2k_B T) = z_0/z + 2 \cos[\pi/(N + 2)]. \tag{19}$$

In the limit $N \to \infty$ the bulk Curie temperature T_B is determined by

$$2\Omega \coth(\Omega/2k_B T_B) = n_0 J \qquad (20)$$

where $n_0 = z_0 + 2z$ is the total number of neighbours. It can be seen that equation (20) has a solution only if $n_0 J \geqslant 2\Omega$.

3. Curie temperature of ferroelectric films with multi-surface modification

As an example, we consider an (l, n, l) film consisting of l top surface layers, n bulk layers and l bottom surface layers and study three models. In model I, we assume that pseudo-spins lie on a simple cubic lattice and that the transverse field $\Omega_i = \Omega$. The coupling strength in a surface layer is denoted by J_s and that in a bulk layer or between successive layers is denoted by J. Then the transfer matrix (equation (8)) reduces to two different types of matrix

$$P = \begin{pmatrix} X & -1 \\ 1 & 0 \end{pmatrix} \qquad Q = \begin{pmatrix} Y & -1 \\ 1 & 0 \end{pmatrix} \qquad (21)$$

and the total transfer matrix

$$R = P^{l-1} Q^n P^{l-1}. \qquad (22)$$

Here $X = \tau - 4J_s/J$ and $Y = \tau - 4$. The nonlinear equation (10) for Curie temperature thus reduces to

$$R_{11} X^2 + (R_{12} - R_{21}) X - R_{22} = 0. \qquad (23)$$

The matrix elements of R can be obtained explicitly from equations (13) as

$$R_{11} = V_{l-1}^2 W_n X^2 Y - V_{l-1}^2 W_{n-1} X^2 - 2V_{l-1} V_{l-2} W_n X Y + 2(V_{l-1} V_{l-2} W_{n-1} - V_{l-1}^2 W_n) X$$
$$+ V_{l-2}^2 W_n Y + V_{l-1}^2 W_{n-1} + 2V_{l-1} V_{l-2} W_n - V_{l-2}^2 W_{n-1}$$

$$R_{12} = -R_{21} = -V_{l-1}^2 W_n X Y + (V_{l-1}^2 W_{n-1} + V_{l-1} V_{l-2} W_n) X + V_{l-1} V_{l-2} W_n Y$$
$$+ V_{l-1}^2 W_n - 2V_{l-1} V_{l-2} W_{n-1} - V_{l-2}^2 W_n$$

$$R_{22} = -V_{l-1}^2 W_n Y + V_{l-1}^2 W_{n-1} + 2V_{l-1} V_{l-2} W_n - V_{l-2}^2 W_{n-1}. \qquad (24)$$

Here $V_l = (\alpha_+^l - \alpha_-^l)/(\alpha_+ - \alpha_-)$, $W_n = (\beta_+^n - \beta_-^n)/(\beta_+ - \beta_-)$, $\alpha_\pm = (X \pm \sqrt{X^2 - 4})/2$ and $\beta_\pm = (Y \pm \sqrt{Y^2 - 4})/2$.

For the special case of $l = 1$, equation (23) reduces to

$$W_{n+1} X^2 - 2W_n X + W_{n-1} = 0 \qquad (25)$$

which is the same as that of [30] for the structure with one top and one bottom surface layer. In obtaining equation (25), we have used equation (15).

Equation (23) can be numerically solved for arbitrary l and n. Figure 1 shows the reduced Curie temperature $t_C = k_B T_C/J$ as a function of J_s/J for films (l, n, l) with fixed bulk layer numbers $n = 1$ but different surface layer numbers l. Curie temperature increases with increasing l for larger J_s/J, while it is almost independent of l when J_s/J is sufficiently small. Figure 2 shows t_C against J_s/J for films $(3, n, 3)$ with different bulk layer numbers. The four curves n merge into one curve for larger J_s/J, i.e., the Curie temperatures are insensitive to the bulk layer numbers n in this case. In contrast, Curie temperature depends strongly on number n for smaller J_s/J (say $J_s/J < 1$) and t_C increases as n increases.

Only one type of surface modification, the modification of surface exchange constant J_s, is taken into account in the above discussion. Next we study model II including the modification of surface transverse field. Let Ω_s and Ω denote transverse field in surface and bulk
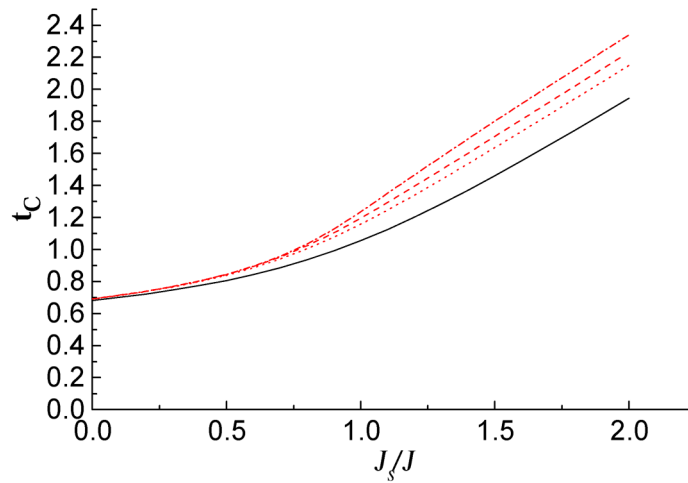
Figure 1. The reduced Curie temperature t_C against J_s/J in model I for films $(l, 1, l)$ with $l = 1$ (solid line); $l = 2$ (dotted line), $l = 3$ (dashed line) and $l = 10$ (dot–dashed line). The parameter $\Omega/J = 2.0$.
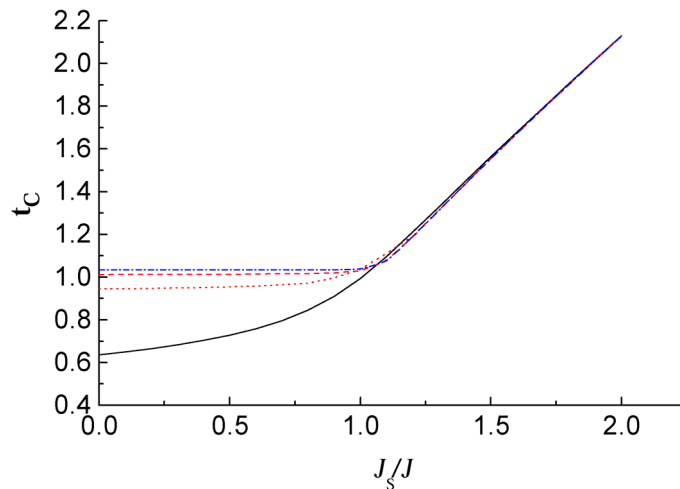

Figure 2. The same as figure 1, but for films $(3, n, 3)$ with $n = 2$ (solid line), $n = 5$ (dotted line), $n = 10$ (dashed line) and $n = 20$ (dot–dashed line). The parameter $\Omega/J = 2.5$.

layers respectively. The nonlinear equations for Curie temperature are still the equations (23) and (24) except for the change of the element X from $\tau - 4J_s/J$ to $\tau_s - 4J_s/J$, where $\tau_s = (2\Omega_s/J) \coth(\Omega_s/2k_B T)$. In figure 3, we give the Curie temperature against Ω_s/J. The Curie temperature decreases as Ω_s/J increases. The transverse field causes a reduction in the Curie temperatures of the film.

Now we consider a more realistic model, model III, in which we assume $J_{ij} = J_s$ for both sites in surface layers, $J_{ij} = J$ for both sites in bulk layers, and $J_{ij} = J_{BS} = \sqrt{J_s J}$ between interface layers. The transverse fields $\Omega_i = \Omega_s$ for sites in the surface layers, $\Omega_i = \Omega$ for sites in the bulk layers and $\Omega_i = \Omega_{BS} = \sqrt{\Omega_s \Omega}$ in the interface layers. The total transfer matrix
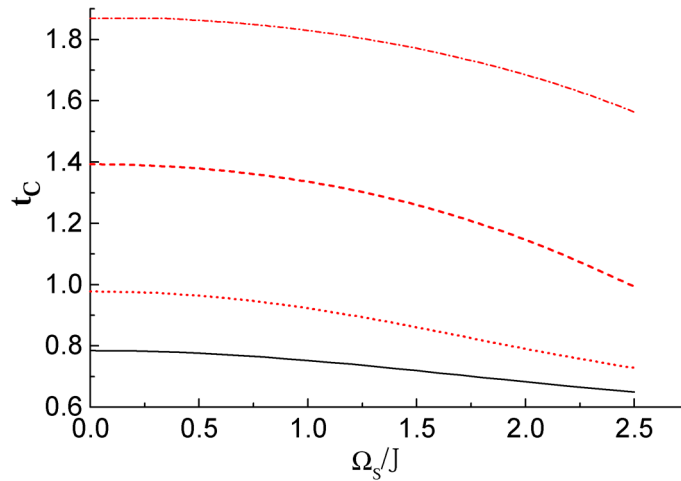
Figure 3. The reduced Curie temperature against Ω_s/J in model II for films $(3, 2, 3)$ with $J_s/J = 0.1$ (solid line), $J_s/J = 0.5$ (dotted line), $J_s/J = 1.0$ (dashed line) and $J_s/J = 1.5$ (dot–dashed line). The parameter $\Omega/J = 2.5$.

for model III becomes

$$R = M_S^{l-2} M_{SB} M_B^{n-2} M_{BS} M_S^{l-2} \tag{26}$$

where

$$M_S = \begin{pmatrix} \tau_s J/J_s & -1 \\ 1 & 0 \end{pmatrix}$$

$$M_B = \begin{pmatrix} \tau & -1 \\ 1 & 0 \end{pmatrix}$$

$$M_{BS} = M_l M_{l-1} = \begin{pmatrix} (\tau_{BS} - 4)(\tau_{BS} - 4J_s/J)J/J_{BS} & -(\tau_{BS} - 4)J_s/J_{BS} \\ (\tau_{BS} - 4J_s/J)J/J_{BS} & -J_s/J_{BS} \end{pmatrix}$$

$$M_{SB} = M_{l+n} M_{l+n-1}$$
$$= \begin{pmatrix} (\tau_{BS} - 4)(\tau_{BS} - 4J_s/J)J^2/(J_s J_{BS}) & -(\tau_{BS} - 4J_s/J)J^2/(J_s J_{BS}) \\ (\tau_{BS} - 4)J/J_{BS} & -J/J_{BS} \end{pmatrix} \tag{27}$$

and $\tau_{BS} = 2\Omega_{BS}/J \coth(\Omega_{BS}/2k_B T)$. For film $(2, 2, 2)$, the transfer matrix reduces to $M_{SB} M_{BS}$. From equations (10) and (27), we can numerically calculate the Curie temperature of (l, n, l) films. In order to compare with the results of model II, we consider the Curie temperature against Ω_s/J and choose parameters the same as those in figure 3. The results are given in figure 4. For small Ω_s/J (say $\Omega_s/J = 0.1$), the Curie temperatures in model III are larger than those in model II. It is clear that the results are qualitatively consistent with those of model II, while they are quantitatively different. For large Ω_s/J (say $\Omega_s/J = 2.5$) and $J_s/J = 0.1$, the Curie temperatures of model III are smaller than those in model II. It can be seen from both figure 3 and figure 4 that the Curie temperature increases as J_s/J increases. Figure 5 gives the Curie temperature against surface layer number l. The solid line in the figure corresponds to the Curie temperature t_C^S of the bulk system with $J_{ij} = J_s$ and $\Omega_{ij} = \Omega_s$. Let $\Omega \rightarrow \Omega_s$, $J \rightarrow J_s$ in equation (20): the temperature t_C^S can be calculated. As seen from the figure, the Curie temperature increases with the increase of surface layer number and approach asymptotically to the bulk temperature t_C^S.
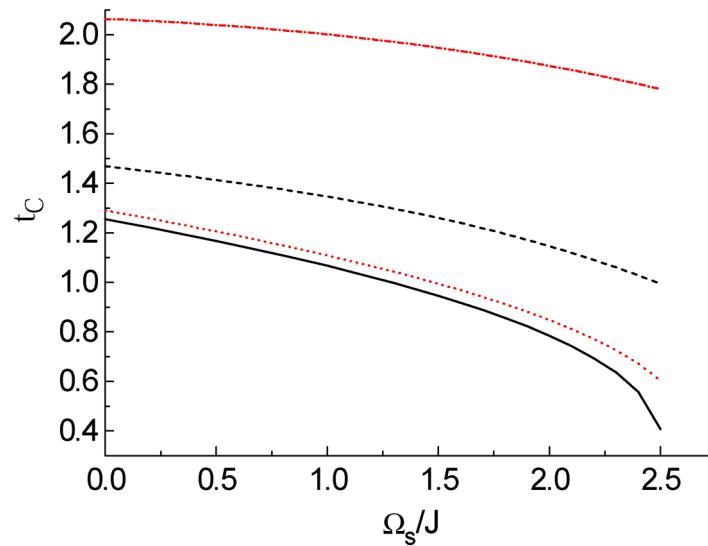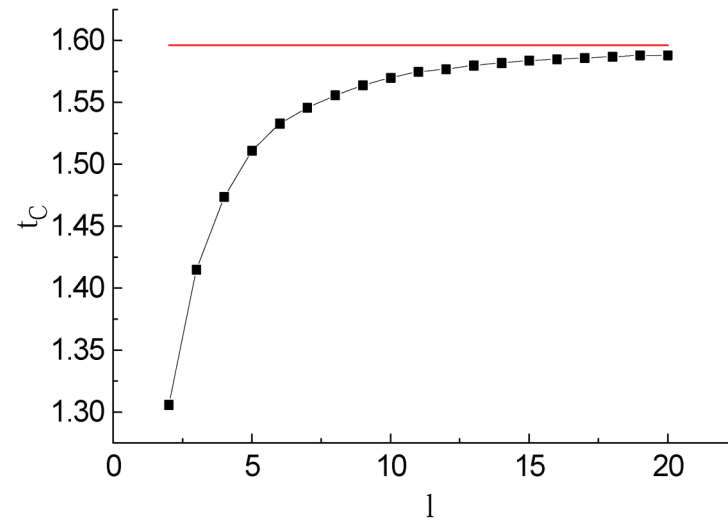
Figure 4. The same as figure 3, but for model III.

Figure 5. The reduced Curie temperature against l in model III. The parameters $\Omega_s = 2.0$, $\Omega = 2.5$, $J_s = 1.2$ and $n = 5$.

4. Conclusions

By making use of the transfer matrix method, an analytical and general nonlinear equation for Curie temperature of ferroelectric films with arbitrary exchange constant J_{ij} and transverse field Ω_i has been derived based on the TIM. The dependence of Curie temperature on surface layer numbers, bulk layer numbers, surface exchange constants, surface transverse fields and bulk transverse fields can be easily studied by the nonlinear equation. As an example, we study three models and investigate the effects of multi-surface modification on Curie temperature of symmetric ferroelectric films (l, n, l). In addition, the method proposed here can be applied to

phase transition of both infinite and finite ferroelectric superlattices. It has a favourable point because of the simplicity of the numerical calculations.

References

[1] Landau L D and Lifshitz E M 1960 *Electrodynamics of Continuous Media* (New York: Pergamon)
[2] de Gennes P D 1966 *Superconductivity of Metals and Alloys* (New York: Benjamin)
[3] Kretscgner R and Binder K 1979 *Phys. Rev.* B **20** 1065
[4] Ishikawa K, Yoshikawa K and Okad N 1988 *Phys. Rev.* B **37** 5852
[5] Batra I P,Wurfel P and Silverman B D 1973 *Phys. Rev. Lett.* B **30** 384
[6] Binder K 1981 *Ferroelectrics* **35** 99
[7] Binder K 1987 *Ferroelectrics* **73** 43
[8] Tilley D R and Zeks B 1984 *Solid State Commun.* **49** 823
[9] Bell A J and Moulson A J 1984 *Ferroelectrics* **54** 147
[10] Cottam M G, Tilley D R and Zeks B 1984 *J. Phys. C: Solid State Phys.* **17** 1793
[11] Scott J F, Duiker H M, Beale P D, Pouligny B, Dimmler K, Parris M, Butler D and Eaton S 1988 *Physica* B **150** 160
[12] Kanata T, Yoshikawa T and Kubota K 1987 *Solid State Commun.* **62** 765
[13] Blinc R and Zeks B 1974 *Soft Modes in Ferroelectrics and Antiferroelectrics* (Amsterdam: North-Holland)
[14] Aguilera-Granja F and Moran-Lopez J L 1990 *Solid State Commun.* **74** 155
[15] Elliott R J and Young A P 1974 *Ferroelectrics* **7** 23
[16] Wang C L, Smith S R P and Tilley D R 1995 *J. Magn. Magn. Mater.* **140–144** 1729
[17] Wang X Z and Zhao Y 1993 *Physica* A **193** 33
[18] Stinchcombe R B 1973 *J. Phys. C: Solid State Phys.* **6** 2459
[19] McCauley D, Newnham R E and Randall C A 1998 *J. Am. Ceram. Soc.* **81** 979
[20] Zhong W L 1998 *J. Korea Phys. Soc.* **32** S265
[21] Swartz S L and Wood V E 1992 *Condens. Matter News* **1** 4
[22] Jaccard A, Kanzig W and Peter M 1953 *Helv. Phys. Acta* **26** 521
[23] Anliker M, Brugger H R and Kanzig W 1954 *Helv. Phys. Acta* **27** 99
[24] Kanata T, Yoshikawa K and Kubota K 1987 *Solid State Commun.* **62** 765
[25] Ishikawa K, Yoshikawa K and Okada N 1988 *Phys. Rev.* B **37** 5852
[26] de Gennes P G 1963 *Solid State Commun.* **1** 132
[27] Sarmento E F and Tucker 1993 *J. Magn. Magn. Mater.* **118** 133
[28] Elliott R J, Harley R T, Hayes W and Smith S R P 1972 *Proc. R. Soc.* A **328** 217
[29] Wang C L, Zhong W L and Zhang P L 1992 *J. Phys.: Condens. Matter* **3** 4743
[30] Sy H K 1993 *J. Phys.: Condens. Matter* **5** 1213
[31] Saber M, Ainane A, Dujardin F and Stebe B 1999 *Phys. Rev.* B **59** 6908
[32] Barnas J 1992 *Phys. Rev.* B **45** 10 427
[33] Yariv A and Yeh P 1984 *Optical Waves in Crystals* (New York: Wiley)