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**Curie Temperature for a Finite Alternating Ferroelectric Superlattice**

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We examine the critical behavior of a finite alternating ferroelectric superlattice based on the transverse Ising model. By the transfer matrix method we derive analytical equations for the Curie temperature of the superlattice. Numerical results are obtained for the dependence of the Curie temperature on the thickness and exchange constants of the superlattice. The effect of transverse field on the Curie temperature is also investigated.

1. Introduction

Possibly because of the great difficulty of growing well characterized samples, only few experimental studies of ferroelectric superlattices have been published in recent years [1 to 6]. Some exploratory theoretical work on ferroelectric superlattices has appeared [7 to 9]. Their starting point is Ginzburg-Landau phenomenological theory. On the microscopic level, the transverse Ising model (TIM) [10 to 13] was used to study ferroelectric superlattices under mean field theory [14 to 16] or effective field theory [17]. It has been proved that in the semi-infinite TIM, there is a localized surface spin wave [18]. The surface diagram [19] and the surface magnetism in the presence of a disordered surface [20] were also obtained from this model.

The TIM describes the hydrogen-bonded ferroelectrics, such as KH\(_2\)PO\(_4\), where the proton sits in one or other minimum of a double well, the transverse-field term represents the ability of the proton to tunnel between the two minima, and the exchange term represents the correlation energy of possible proton arrangements [10, 21]. The model also applies to ferromagnets with strong uniaxial anisotropy such as Dy(C\(_2\)H\(_5\)SO\(_4\))\(_3\) · 9H\(_2\)O, in a transverse field [22]. The spin is pseudo-spin when TIM describes ferroelectrics, while the spin is real spin when TIM describes ferromagnets.

Huang et al. have investigated the magnetic properties of epitaxial thin films of Co, Ni, and their alloys grown on Cu(100) and Cu(111) and found that the Curie temperature is higher for the same films of a given thickness on Cu(111) than on Cu(100) [23]. Willis has presented experimental evidence of a cross-over in dimensionality occurring at a finite critical film thickness, determined by a finite sized quantization of the electro-

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nomic states [24]. He also presented evidence that configurational entropy destroys long magnetic order driving the Curie temperature to zero in the single monolayer thickness limit. It is now possible to grow very thin films and even monolayers. The two additional examples are: iron (Fe) monolayer has been grown on gold (Au) [25] and gadolinium (Gd) monolayer has been grown on tungsten (W) [26]. It is now reasonable to study theoretically the superlattice in which the atoms vary from one monolayer to another.

Recently Bovensiepen et al. reported the ac susceptibility $\chi$ of ultrathin Co and Ni layers coupled indirectly across a Cu spacer [27]. A single $\chi$ maximum (singularity) or two $\chi$ maxima (one singularity, one resonant-like signal) appear near the respective Curie temperature of bare layers. Hernando et al. reported that the dependence of Ni Curie temperature on the Ni thickness in Co–Ni and Ag–Ni multilayers [28]. It is shown that the Curie temperature increases as the Ni thickness decreases. The Curie temperature is a basic magnetic observable and it is meaningful to investigate the Curie temperature in thin films and superlattices.

In this paper, we will study the ferroelectric superlattice which alternates as ABAB...AB (Model I) or ABABA...BA (Model II). By use of the transfer matrix method, we obtain an analytical equation for the Curie temperature. Some numerical results are given.

2. Curie Temperature

We start with the TIM [10, 14 to 16]

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

where $S_{ir}^x, S_{ir}^z$ 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 $\Omega_i$ is dependent only on layer index and consider the interaction between neighboring sites.

The spin average $\langle S_i \rangle$ obtained from the mean field theory [14 to 16], is

$$\langle S_i \rangle = \frac{H_i}{2|H_i|} \tanh \left( \frac{|H_i|}{2k_B T} \right),$$

where $H_i \left( \Omega_i, 0, \sum_j J_{ij} \langle S_j^z \rangle \right)$ is the mean field acting on the $i$-th spin, $k_B$ is the Boltzmann constant and $T$ is the temperature.

At a temperature close and below the Curie temperature, $\langle S_i^x \rangle$ and $\langle S_i^z \rangle$ are small, $|H_i| \approx \Omega_i$, Eq. (2) can be approximated as

$$\langle S_i^x \rangle = \frac{1}{2} \tanh \left( \frac{\Omega_i}{2k_B T} \right),$$

$$\langle S_i^z \rangle = \frac{1}{2\Omega_i} \tanh \left( \frac{\Omega_i}{2k_B T} \right) \left[ z_0 J_{ii} \langle S_i^z \rangle + z(J_{i,i+1} \langle S_{i+1}^z \rangle + J_{i,i-1} \langle S_{i-1}^z \rangle) \right].$$

Here $z_0$ and $z$ are the numbers of nearest neighbors in a certain plane and between successive planes, respectively.

Let us rewrite Eq. (4) in matrix form in analogy with Ref. [29]:

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

(5)
with $M_i$ as the transfer matrix defined by

$$M_i = \begin{pmatrix}
\frac{(\tau_i - z_0 J_{ii})/(zJ_{i,i+1})}{1} & -J_{i,i+1}/J_{i,i+1} \\
1 & 0
\end{pmatrix},$$

(6)

where $m_i = \langle S_i^z \rangle$ and $\tau_i = 2\Omega_i/(zJ_{i+1,i}) \coth [\Omega_i/(2k_B T)]$.

We consider a ferroelectric superlattice which alternates as ABAB...AB and assume that the lattice has $2l$ layers. The thickness of each layer is a few lattice constants and is of nm regime. Layers $n = 0, 2, ..., 2l-2$ consist of atoms of type A with exchange constant $J_A$ and transverse field $\Omega_A$, whereas layers $n = 1, 3, ..., 2l-1$ consist of atoms of type B with exchange constant $J_B$ and transverse field $\Omega_B$. The exchange constants between all successive layers are given by $J_{AB}$. In this case, the transfer matrix reduces to two types:

$$M_A = \begin{pmatrix}
X_A & -1 \\
1 & 0
\end{pmatrix}, \quad M_B = \begin{pmatrix}
X_B & -1 \\
1 & 0
\end{pmatrix},$$

(7)

where $X_A = \tau_A - J_A, X_B = \tau_B - J_B, J_A = z_0 J_A/(zJ_{AB}), J_B = z_0 J_B/(zJ_{AB}), \quad \tau_A = 2\Omega_A/(zJ_{AB}) \coth [\Omega_A/(2k_B T)],$ and $\tau_B = 2\Omega_B/(zJ_{AB}) \coth [\Omega_B/(2k_B T)]$.

From Eq. (5), we get

$$\begin{pmatrix}
m_{2l-1} \\
m_{2l-2}
\end{pmatrix} = R \begin{pmatrix}
m_1 \\
m_0
\end{pmatrix},$$

(8)

where $R = M_A^{-1}(M_AB = M_AM_B)$ represents successive multiplication of the transfer matrices $M_i$. From the above equation and the following equations

$$m_1 = X_A m_0, \quad m_{2l-2} = X_B m_{2l-1},$$

(9)

we obtain the equation for the Curie temperature of the superlattice as

$$R_{11}X_AX_B + R_{12}X_B - R_{21}X_A - R_{22} = 0.$$  

(10)

Note that det $(M_{AB}) = 1$, the matrix $R$ can be written as [30,31]

$$R = U_{l-1}M_{AB} - U_{l-2}I,$$

(11)

where $I$ is the unit matrix, $U_N = (\lambda_+^N - \lambda_-^N)/(\lambda_+ - \lambda_-)$, and

$$\lambda_\pm = \frac{1}{2}(X_AX_B - 2 \pm \sqrt{X_A^2 X_B^2 - 4X_A X_B}).$$

(12)

From Eqs. (7) and (12), the matrix elements of the matrix $R$ are

$$R_{11} = U_l + U_{l-1}, \quad R_{12} = -X_A U_{l-1},$$

$$R_{21} = X_B U_{l-1}, \quad R_{22} = -(U_{l-1} + U_{l-2}).$$

(13)

In the derivation of Eq. (13), we have used the following identity

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

(14)

Substituting Eq. (13) into Eq. (10) and using Eq. (14), we obtain

$$U_{l+1} + U_l = 0.$$  

(15)

The above equation is the equation for the Curie temperature of the superlattice which alternates as ABAB... AB.
Next we consider Model II, the superlattice which alternates as ABA...BA and assume that the lattice has \(2l + 1\) layers. The total transfer matrix \(R\) becomes

\[
R = M_B M_{AB}^{l-1} = \begin{pmatrix} X_B U_l & -U_l - U_{l-1} \\ U_l + U_{l-1} & -X_A U_{l-1} \end{pmatrix},
\]

and the equation for the Curie temperature is formally written as

\[
R_{11}X_A^2 + (R_{12} - R_{21}) X_A - R_{22} = 0.
\]

Substituting the matrix elements of \(R\) into Eq. (17) and using Eq. (14), we obtain

\[
U_{l+1} = 0.
\]

The above equation is the equation for the Curie temperature of the superlattice which alternates as ABA...BA.

\(U_{l+1}\) can be rewritten as [32]

\[
U_{l+1} = \sin [(l + 1) \theta]/\sin \theta
\]

for \(X_A X_B \leq 4\). Here \(\theta = \arccos(X_A X_B/2 - 1)\). For \(X_A X_B > 4\), \(\theta\) becomes \(i\phi\), and the trigonometric functions become hyperbolic functions of \(\phi\).

Equation (18) gives

\[
X_A X_B - 2 = 2 \cos [\pi/(l + 1)].
\]

Similarly, Eq. (15) gives

\[
X_A X_B - 2 = 2 \cos [2\pi/(2l + 1)].
\]

We let \(\Omega_A = \Omega_B = \Omega\) (the case \(\Omega_A \neq \Omega_B\) will be considered later). Thus \(X_A = \tau - j_A\), \(X_B = \tau - j_B\), and \(\tau = \tau_A = \tau_B = 2\Omega/(zJ_{AB}) \coth(\Omega/(2k_B T))\). We can analytically derive the equations for the reduced Curie temperature \(t_C = k_B T_C/(zJ_{AB})\) as

\[
t_C = \frac{1}{2} \omega/\text{arccoth} \left\{ \left\{ j_A + j_B + \left( j_A - j_B \right)^2 + 16 \cos \left( \frac{\pi}{2l + 1} \right)^2 \right\}^{1/2} \right\} / (4\omega)
\]

for Model I,

\[
t_C = \frac{1}{2} \omega/\text{arccoth} \left\{ \left\{ j_A + j_B + \left( j_A - j_B \right)^2 + 16 \cos \left( \frac{\pi}{2l + 2} \right)^2 \right\}^{1/2} \right\} / (4\omega)
\]

for Model II,

where \(\omega = \Omega/(zJ_{AB})\) is the reduced transverse field.

The Curie temperature for infinite superlattice is obtained by taking the limit \(l \to \infty\) in the above equation and is given by

\[
t_0 = \frac{1}{2} \omega/\text{arccoth} \left\{ \left\{ j_A + j_B + \left[ (j_A - j_B)^2 + 16 \right]^{1/2} \right\} / (4\omega) \right\}
\]

3. Numerical Results

In Fig. 1, we show the dependence of the Curie temperature on \(l\) for both model I and model II. The Curie temperature increases as \(l\) increases. For small \(l\), the Curie tem-
temperatures in model II are larger than those in model I since there are $2l + 1$ layers in model II and $2l$ layers in model I, i.e., the superlattice of model II is thicker than model I. The Curie temperature of the finite superlattice is always less than that of the corresponding infinite superlattice and reaches the last one for large values of $l$. This fact can also be seen from Eqs. (22) to (24). Notice that the Curie temperature of the corresponding infinite superlattices is reached quite rapidly. This limiting value is approached faster in the case of model II. Figure 2 shows the dependence of the Curie temperature on $j_A$ for different $\omega$. The Curie temperature increases with the increase of $j_A$ and decreases with the increase of the reduced transverse field $\omega$. When $j_A$ is large enough, the Curie temperature increases nearly linearly with the increase of $j_A$.

In Fig. 3, we present the Curie temperature of the superlattice as a function of the strength of the transverse field $\omega$ for different thickness: $l = 1, 3$, and infinite. We find that there exist a critical transverse field $\omega_c$, when $\omega > \omega_c$ at any temperature, there cannot be ferroelectric phase. At the critical transverse field, the critical temperature reduces to zero. The Curie temperature of a finite superlattice is always less than that of a corresponding infinite superlattice, and it increases with the increase of $l$ to approach asymptotically $t_C$ for large values of $l$.

Fig. 1. The dependence of the Curie temperature $t_C/t_0$ of a finite ferroelectric superlattice on the thickness $l$ for both model I and II. The parameters $\omega = 0.5$, $j_A = 2$, and $j_B = 1$.

Fig. 2. The dependence of the Curie temperature on $j_A$ for different $\omega$ (Model II). The parameter $j_B = 1$. 
Now we consider the case $\Omega_A \neq \Omega_B$. The equations for the Curie temperature for superlattices are obtained as

$$2\omega_A \omega_B \coth \frac{\omega_A}{2l_C} \coth \frac{\omega_B}{2l_C} - j_A \omega_B \coth \frac{\omega_B}{2l_C} - j_B \omega_A \coth \frac{\omega_B}{2l_C} + \frac{1}{2} j_A j_B$$

$$= 1 + \cos \left( \frac{2\pi}{2l+1} \right) \quad \text{for Model I}, \quad (25)$$

$$2\omega_A \omega_B \coth \frac{\omega_A}{2l_C} \coth \frac{\omega_B}{2l_C} - j_A \omega_B \coth \frac{\omega_B}{2l_C} - j_B \omega_A \coth \frac{\omega_B}{2l_C} + \frac{1}{2} j_A j_B$$

$$= 1 + \cos \left( \frac{\pi}{l+1} \right) \quad \text{for Model II}, \quad (26)$$

where $\omega_A = \Omega_A/(\pi J_{AB})$ and $\omega_B = \Omega_B/(\pi J_{AB})$. When $\omega_A = \omega_B$, the Eqs. (25) and (26) reduce to Eqs. (22) and (23) as we expected. The Curie temperature can be determined from the above two nonlinear equations. Figure 4 gives the dependence of the Curie temperature on $j_A$ for different $\omega_A$. We can see that the Curie temperature decreases with the increase of the reduced transverse field $\omega_A$. This is similar to that in Fig. 2.

Fig. 3. The Curie temperature $t_C$ versus $\omega$ for $l = 1, 3$ and infinite (Model I). The parameters $j_A = 2$, and $j_B = 1$

Fig. 4. The dependence of the Curie temperature on $j_A$ for different $\omega_A$ (Model I). The parameters $j_B = 1$, $\omega_B = 0.3$ and $l = 10$
4. Summary

In summary, we derive the analytical equations for the Curie temperature of a ferroelectric superlattice which alternates as ABAB...AB or ABA...BA by use of the transfer matrix method. We give the numerical results for the dependence of the Curie temperature on the thickness and exchange constants of the superlattice. The effect of the transverse field on the Curie temperature is also investigated. We hope the present work will stimulate other theoretical studies and will have relevance to some future experiments on ferroelectric superlattices.

References