Magnetization reorientation and anisotropy in ultrathin magnetic films

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The temperature dependence of spontaneous magnetization for every monolayer, as well as of various anisotropies in an ultrathin ferromagnetic film, is investigated by means of the Green-function technique. The Hamiltonian is based on the Heisenberg model with the surface anisotropy and demagnetization included. A microscopic theory valid in the whole temperature range is then developed to calculate the energy spectrum, spontaneous magnetization, and various anisotropies of the film. The transition temperature for the reorientation transition between perpendicular and in-plane magnetization, as well as the Curie temperature, is calculated as a function of L, the number of monolayers in the film. Numerical results for $L=1-8$ are presented. It is shown that our results are able to account for experimental data that are available for ultrathin Fe films.

I. INTRODUCTION

One of the most interesting discoveries in magnetic research in recent years is perhaps the reorientation of the magnetization observed in ultrathin magnetic films. A reorientation transition (RT) of the magnetization between perpendicular and in-plane directions was observed at the transition temperature T_R below the Curie temperature T_C in films of a few monolayers (ML) of Fe, Co, and Ni on Cu or Ag substrates. It depends, however, strongly on the materials as well as on the sample preparation. There are ordinarily two types of reorientation when the temperature increases: the transition of the magnetization orientation in Fe films from a perpendicular direction to an in-plane direction[1–9] and the reorientation in Ni films from an in-plane to perpendicular direction[10–14] as the film thickness increases. It is also possible that the magnetization changes from perpendicular to in-plane with increasing temperature but decreasing thickness of the film.[15,16]

Theoretically, the reorientation of magnetization in magnetic films may be qualitatively understood by considerations of the competing shape and uniaxial anisotropy in the mean-field theory,[16–19] the renormalization-group method,[20] the Monte Carlo simulation,[21] the spin-wave dispersion,[22] and the stripe domain structures.[23] It is also found that the transition is mediated by a strong reduction of the surface magnetization relative to the inner ML.[17,18,24] More quantitative calculations carried out by means of various techniques such as the renormalization-group, mean-field approximation, and Monte Carlo simulation in different regions of temperature yield different results.[25] Furthermore, the first nonvanishing magnetic anisotropy is calculated in the random-phase approximation,[26] the anisotropy-flow concept is utilized in the anisotropic space,[27] and the magnetic dipole coupling and a layer-dependent anisotropy are included in the Hubbard model.[24] For an ideal face-centered-cubic (fcc) lattice, a transition to in-plane anisotropy is found in a film of 8 ML.[28]

In dealing with the reorientation transition, the mean-field theory can only provide a qualitative description in a limited temperature range, and cannot be applied in the low-temperature limit nor in the neighborhood of the Curie temperature. In this paper, we develop a microscopic theory to calculate various anisotropies and to investigate phase transitions in ultrathin ferromagnetic Fe films with fcc lattice structures by means of the retarded Green-function technique, which is valid in the whole temperature range. A forthcoming paper will be devoted to the treatment of transitions in Ni films.

The Green-function method has been successfully applied to treat ferromagnetism,[29–31] antiferromagnetism,[32,33] and ferrimagnetism.[34] The Curie temperature T_C, the spontaneous magnetization M_s normal to the plane, and the transition temperature T_R are calculated in this paper for films consisting of $L=1-8$ ML. Furthermore, the surface- and shape-anisotropies K_s and K_d are expressed in terms of the statistical average of spin operators and are calculated as functions of the temperature T for various L values. The model Hamiltonian we employ in this work includes the Heisenberg exchange term plus a surface anisotropy term and a demagnetization term. The degree of surface anisotropy is measured by D_s, and that of the shape anisotropy is described by the magnetic dipole demagnetization.[35] Strong dependence of the perpendicular remanence (PR) on the temperature and film thickness is found. Conditions for the existence of PR are determined, and agreement with experiments is demonstrated.

In Sec. II, we review briefly the Green-function formalism and outline the calculation procedure. Both the spontaneous magnetization of individual monolayers and the Curie temperature for a film of L ML are calculated in Sec. III, where $L=1-8$. The various anisotropies are found as a function of T for various L values in Sec. IV. Relations between the PR stability and anisotropy are also studied here. Moreover, the thickness dependence of the reorientation transition tempera-

ture $T_R(L)$ is determined. Finally, a few remarks are given in Sec. V.

II. THEORY

Consider a magnetic film of fcc lattice with (001) surfaces perpendicular to the z axis. It has L ML and each ML contains $N\times N$ atomic spins where $N\to\infty$. The spatial coordinates (x, y, z) has its origin on the left surface of the film, and the spin-quantization coordinates is (X, Y, Z) with the quantization axis Z. The two coordinates coincide if the easy anisotropy is perpendicular to the surface, and $Z\|y$, $X\|z$, $Y\|x$ if the easy anisotropy is in-plane. The Hamiltonian is assumed to take the form

$$H=-\tfrac{1}{2}\sum_{\langle ij\rangle} J_{ij}\vec{S}_i\cdot\vec{S}_j-\sum_i D_i(S_i^z)^2+\frac{\mu^2}{2V}N_z\sum_{i,j} S_i^zS_j^z. \tag{1}$$

The first term is simply the Heisenberg exchange energy and $\langle ij\rangle$ indicates that the sum is taken over nearest neighbors only. The second term represents the anisotropic surface energy due to the coupling of the crystal field and spin-orbit interaction,[36] and the parameter D_i characterizes the surface anisotropy. The last term describes approximately the shape anisotropy due to the demagnetization energy of uniform magnetization,[35] which is originated from the dipole-dipole interaction. Although the dipole interaction is generally two or three orders of magnitude weaker than the exchange coupling, it may become very important because of its long-range nature. In particular, it leads to the demagnetization factors. For Fe films, we choose $N_x=N_y=0$ for in-plane and $N_z=4\pi$ for out-of-plane, which is consistent with the approximation. We assume in the following, for simplicity, $J_{ij}=J$ for the coupling constant between all nearest neighbors. The volume of the film is denoted by V and μ is the magnetic moment.

To calculate the relative spontaneous magnetization σ_ν for an individual ML labeled by ν in the film, we start with the retarded Green function

$$\begin{aligned}G_{ij}(t-t')&=\langle\langle S_i^+(t);[S_j^z(t')]^nS_j^-(t')\rangle\rangle\\&=-i\theta(t-t')\langle S_i^+(t)[S_j^z(t')]^n\\&\quad\times S_j^-(t')-[S_j^z(t')]^nS_j^-(t')S_i^+(t)\rangle\\&=\int_{-\infty}^{\infty}G_{ij}(\omega)\exp[-i\omega(t-t')]d\omega,\end{aligned}\tag{2}$$

where $n=2S-1$ for an arbitrary spin S. We have employed the spin operators $S_i^+(t)$ at the site i and $[S_j^z(t')]^nS_j^-(t')$ at j, and $S^\pm=S^x\pm iS^y$. As the translation symmetry is broken along the z axis, we introduce the two-dimensional Fourier transform

$$G_{ij}(\omega)=\frac{1}{N^2}\sum_{\boldsymbol{\kappa}} g_{\nu_i\nu_j}(\boldsymbol{\kappa},\omega)e^{i\boldsymbol{\kappa}\cdot(\boldsymbol{\rho}_i-\boldsymbol{\rho}_j)}, \tag{3}$$

where N^2 is the total number of atomic spins in each layer and the g's are Green functions expressed in the Bloch-Wannier representation in which the Bloch function is used in the xy plane and the Wannier function is used in the z direction. $\nu_i(\nu_j)$ labels the monolayer where the magnetic atom i (j) is located. The three-dimensional wave vector and position vector are given by $\mathbf{k}=(\boldsymbol{\kappa},q)$ and $\mathbf{r}=(\boldsymbol{\rho},z)$, respectively, with components $\kappa_x=2\pi n_x/N$ and $\kappa_y=2\pi n_y/N$. As usual, the allowed values of n_x and n_y are $0,\pm1,...,\pm N/2$.

The time-correlated function for two operators A and B at lattice sites i and j is defined as the ensemble average of their product, namely, $F_{ij}(t-t')=\langle A(t)B(t')\rangle$ and $F_{ji}(t'-t)=\langle B(t')A(t)\rangle=F_{ij}(t-t'-i\beta)$, where $\beta=1/k_BT$, and k_B is the Boltzmann constant. They are directly related to the retarded Green function by the equation

$$G_{ij}(t-t')=-i\theta(t-t')[F_{ij}(t-t')-F_{ji}(t'-t)]. \tag{4}$$

The Fourier transform of the correlation function yields the spectral intensity function $J(\omega)$ and $J'(\omega)=e^{-\beta\omega}J(\omega)$; that is,

$$F_{ij}=\int_{-\infty}^{\infty}J(\omega)e^{-i\omega(t-t')}d\omega, \tag{5a}$$

$$F_{ji}=\int_{-\infty}^{\infty}J'(\omega)e^{-i\omega(t-t')}d\omega. \tag{5b}$$

Making use of Eqs. (4) and (5), we can write the Fourier component of $G_{ij}(t-t')$ as

$$\begin{aligned}G_{ij}(E)&=\frac{1}{2\pi}\int_{-\infty}^{\infty}G_{ij}(t-t')e^{i(E+i\varepsilon)(t-t')}d(t-t')\\&=\frac{1}{2\pi i}\int_{-\infty}^{\infty}d(t-t')e^{i(E+i\varepsilon)(t-t')}\\&\quad\times\int_{-\infty}^{\infty}d\omega\,J(\omega)(e^{\beta\omega}-1)e^{-i\omega(t-t')}\\&=\frac{1}{2\pi}\int_{-\infty}^{\infty}J(\omega)(e^{\beta\omega}-1)\frac{d\omega}{E-\omega+i\varepsilon}.\end{aligned}\tag{6}$$

The correlation function F_{ij} can now be expressed in terms of the retarded Green function by considering the difference

$$\begin{aligned}&G_{ij}(\omega+i\varepsilon)-G_{ij}(\omega-i\varepsilon)\\&\quad=\frac{1}{2\pi}\int_{-\infty}^{\infty}(e^{\beta E}-1)J(E)\\&\qquad\times\left(\frac{1}{\omega-E+i\varepsilon}-\frac{1}{\omega-E-i\varepsilon}\right)dE.\end{aligned}\tag{7}$$

If we recall the operator relation

$$\lim_{\varepsilon\to0^+}\frac{1}{x\pm i\varepsilon}\to P\frac{1}{x}\mp i\pi\delta(x), \tag{8}$$

then the integration can easily be evaluated, and Eq. (7) becomes

$$(e^{\beta\omega}-1)J(\omega)=i[G_{ij}(\omega+i\varepsilon)-G_{ij}(\omega-i\varepsilon)]$$
$$=\frac{i}{N^2}\sum_{\boldsymbol{\kappa}}[g_{\nu_i\nu_j}(\boldsymbol{\kappa},\omega+i\varepsilon)-g_{\nu_i\nu_j}(\boldsymbol{\kappa},\omega-i\varepsilon)]e^{i\boldsymbol{\kappa}\cdot(\boldsymbol{\rho}_i-\boldsymbol{\rho}_j)}, \quad (9)$$

where we have made use of Eq. (3) in the last step. Inserting the spectral function $J(\omega)$ from Eq. (9) in (5b), we find the correlation function

$$F_{ji}(t'-t)=\langle[S_j^z(t')]^nS_j^-(t')S_i^+(t)\rangle$$
$$=\frac{i}{N^2}\sum_{\boldsymbol{\kappa}}\int_{-\infty}^{\infty}\frac{d\omega}{e^{\omega/k_BT}-1}\times[g_{\nu_i\nu_j}(\boldsymbol{\kappa},\omega+i\varepsilon)-g_{\nu_i\nu_j}(\boldsymbol{\kappa},\omega-i\varepsilon)]e^{i\boldsymbol{\kappa}\cdot(\boldsymbol{\rho}_i-\boldsymbol{\rho}_j)-i\omega(t-t')}. \quad (10)$$

Because of the translation symmetry in the atomic plane, $\langle(S_j^z)^nS_j^-S_i^+\rangle$ depends only on ν where $\nu=1,2,...,L$ labels the monolayers in the film. Setting $t'=t$ in Eq. (10), we finally obtain

$$\langle(S_j^z)^nS_j^-S_i^+\rangle=\frac{i}{N^2}\sum_{\boldsymbol{\kappa}}\int_{-\infty}^{\infty}\frac{d\omega}{e^{\omega/k_BT}-1}\times[g_{\nu_i\nu_j}(\boldsymbol{\kappa},\omega+i\varepsilon)-g_{\nu_i\nu_j}(\boldsymbol{\kappa},\omega-i\varepsilon)]. \quad (11)$$

The problem is therefore reduced to find the retarded Green function.

III. SPONTANEOUS MAGNETIZATION AND THE CURIE TEMPERATURE

We consider the case of perpendicular easy axis. The ensemble average of spins in an ML is then given by $\langle S_i^z\rangle=\sigma_{\nu_i}S$ due to the translation invariance in the xy plane. The equation of motion for the Fourier components of the retarded Green function takes the form

$$\omega\langle\langle S_i^+;(S_j^z)^nS_j^-\rangle\rangle_\omega=\frac{1}{2\pi}\langle[S_i^+,(S_j^z)^nS_j^-]\rangle\delta_{ij}+\sum_{i'}J_{ii'}\{\langle\langle S_{i'}^zS_i^+;(S_j^z)^nS_j^-\rangle\rangle_\omega-\langle\langle S_i^zS_{i'}^+;(S_j^z)^nS_j^-\rangle\rangle_\omega\}+\sum_{i'}D_{i'}\langle\langle(S_i^+S_{i'}^z+S_{i'}^zS_i^+);(S_j^z)^nS_j^-\rangle\rangle_\omega\delta_{ii'}-\frac{\mu^2}{V}N_z\sum_{i'}\langle\langle S_{i'}^zS_i^+;(S_j^z)^nS_j^-\rangle\rangle_\omega, \quad (12)$$

where the subscript ω indicates the Fourier component of the quantity. To obtain the Green function for practical calculations, we first apply the usual Tyablikov decoupling procedure:[29]

$$\langle\langle S_{i'}^zS_i^+;(S_j^z)^nS_j^-\rangle\rangle_\omega=\langle S_{i'}^z\rangle\langle\langle S_i^+;(S_j^z)^nS_j^-\rangle\rangle_\omega. \quad (13a)$$

The anisotropy term with $i=i'$ is decoupled by assuming

$$\langle\langle(S_i^+S_{i'}^z+S_{i'}^zS_i^+);(S_j^z)^nS_j^-\rangle\rangle_\omega=\Gamma_i\langle S_i^z\rangle\langle\langle S_i^+;(S_j^z)^nS_j^-\rangle\rangle_\omega, \quad (13b)$$

$$\Gamma_i=\langle 3(S_i^z)^2-S(S+1)\rangle/\langle S_i^z\rangle^2, \quad (13c)$$

and the higher-order terms are cut off. Thus Eq. (12) becomes

$$\omega g_{\nu_1\nu_2}(\omega,\boldsymbol{\kappa})=\frac{1}{2\pi}\langle[S_{\nu_1}^+,(S_{\nu_2}^z)^nS_{\nu_2}^-]\rangle\delta_{\nu_1\nu_2}+\sum_{\nu_3}JS\{\sigma_{\nu_3}g_{\nu_1\nu_2}(\boldsymbol{\kappa},\omega)-\sigma_{\nu_1}e^{i\boldsymbol{\kappa}\cdot(\boldsymbol{\rho}_{\nu_3}-\boldsymbol{\rho}_{\nu_1})}g_{\nu_3\nu_2}(\boldsymbol{\kappa},\omega)\}+D_{\nu_1}\Gamma_{\nu_1}S\sigma_{\nu_1}g_{\nu_1\nu_2}(\boldsymbol{\kappa},\omega)-\frac{\mu^2}{V}N_z\sum_{\nu_3}S\sigma_{\nu_3}g_{\nu_1\nu_2}(\boldsymbol{\kappa},\omega), \quad (14)$$

where, as noted previously, the demagnetization factors $N_z=4\pi$. The magnetic moment is given by $\mu=2.2\mu_B$, with the Bohr magneton μ_B.

In order to compare our results with experimental data for Fe films, we apply Eq. (14) to fcc lattices. Every site in an fcc lattice has 12 nearest neighbors, four in-plane and four in each of the neighboring planes. When this is explicitly taken into account, Eq. (14) becomes

$$\sum_{\nu'}(\omega\delta_{\nu\nu'}-P_{\nu\nu'})g_{\nu'\nu_1}(\boldsymbol{\kappa},\omega)=\frac{\delta_{\nu\nu_1}}{2\pi}\langle[S_\nu^+,(S_\nu^z)^nS_\nu^-]\rangle, \quad (15a)$$

where we have defined

$$P_{\nu\nu'}=\{4JS\sigma_\nu[1-\cos(\kappa_x/2)\cos(\kappa_y/2)]+4JS(\sigma_{\nu+1}+\sigma_{\nu-1})+D_\nu\Gamma_\nu S\sigma_\nu-4\pi\mu M_s\}\delta_{\nu\nu'}-2S\sigma_\nu J_{\nu\nu'}[\cos(\kappa_x/2)+\cos(\kappa_y/2)]. \quad (15b)$$

Recall that the relative spontaneous magnetization σ_ν is the same for any ML with $\nu=1,...,L$, while the spontaneous magnetization is $M_s=\mu\Sigma_i\langle S_i^z\rangle/V$, where $V=2N^2Lv$ with the primitive volume $v=a^3/4$ and the lattice constant a. Expressed in terms of the saturated magnetization $M_s(0)=\mu s/v$, we have $M_s=M_s(0)\Sigma_\nu\sigma_\nu/L$. The anisotropy $D_\nu=D_s$ for the surface ML, $\nu=1$, L and $D_\nu=D$ for the inner layers $\nu=2,...,L-1$.

It can be shown by direct substitution that the general solution to Eq. (15a) is

$$g_{\nu\nu}(\boldsymbol{\kappa},\omega)=\frac{1}{2\pi}\langle[S_\nu^+,(S_\nu^z)^nS_\nu^-]\rangle\sum_{\alpha=1}^{L}\frac{U_{\nu\alpha}U_{\alpha\nu}}{\omega-\omega_{\boldsymbol{\kappa}\alpha}}, \quad (16)$$

where U is the solution to the corresponding homogeneous equation

$$\sum_{\mu} (\omega_{\kappa\alpha}\delta_{\nu\mu} - P_{\nu\mu})U_{\mu\alpha} = 0, \tag{17}$$

provided that $\omega_{\kappa\alpha}$ and $U_{\mu\alpha}$ are independent of the ML. It is noted that U has the following properties:

$$\sum_{\alpha} U_{\nu_1\alpha}U_{\nu_2\alpha} = \delta_{\nu_1\nu_2}, \tag{18a}$$

$$\sum_{\nu} U_{\nu\alpha}U_{\nu\alpha'} = \delta_{\alpha\alpha'}. \tag{18b}$$

For a film of L ML, Eq. (17) represents a set of L coupled linear algebraic equations. The eigenvalues are given by the secular equation

$$\begin{vmatrix}
\omega_{\kappa\alpha}-E_1 & J_1 & & & & & \\
J_2 & \omega_{\kappa\alpha}-E_2 & J_2 & & & & \\
 & \cdots & \cdots & \cdots & & & \\
 & & J_\nu & \omega_{\kappa\alpha}-E_\nu & J_\upsilon & & \\
 & & \cdots & \cdots & \cdots & & \\
 & & & J_2 & \omega_{\kappa\alpha}-E_2 & J_2 & \\
 & & & & J_1 & \omega_{\kappa\alpha}-E_1 &
\end{vmatrix} = 0. \tag{19}$$

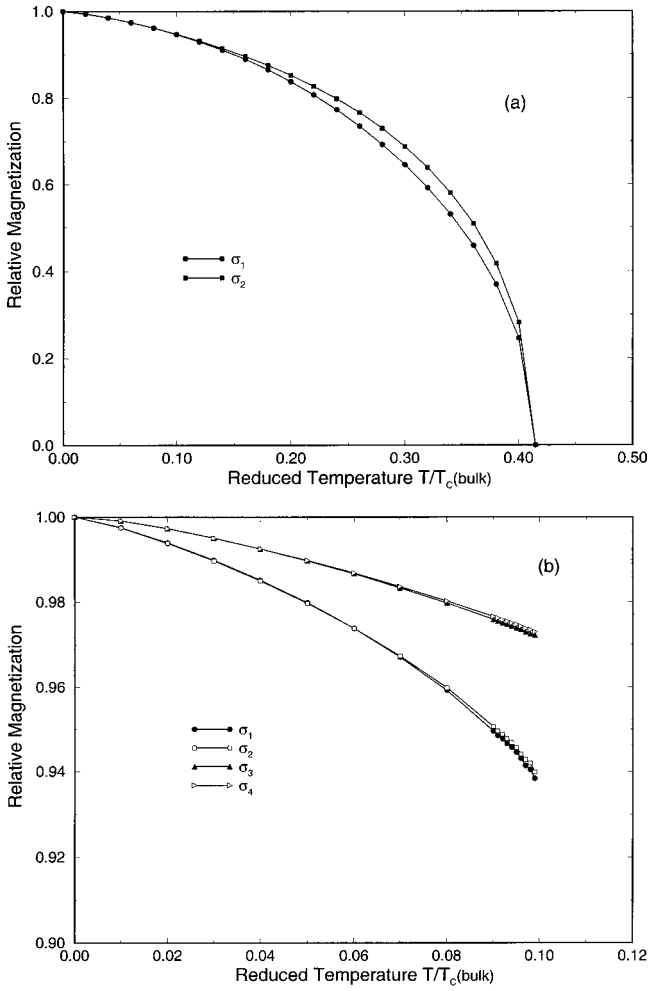

FIG. 1. Relative spontaneous magnetization of individual monolayers versus the reduced temperature for $D_s = 1.1$ meV. (a) $L = 4$ and (b) $L = 7$.

The tridiagonal determinant indicates the reflection symmetry of the film with respect to its central ML as is expected, or $E_\nu = E_{L+1-\nu}$ and $\sigma_\nu = \sigma_{L+1-\nu}$. The energy eigenvalue of an interior ML is

$$E_\nu = 4JS\sigma_\nu[1-\cos(\kappa_x/2)\cos(\kappa_y/2)] + D\Gamma_\nu S\sigma_\nu + 4JS(\sigma_{\nu+1}+\sigma_{\nu-1}) - 4\pi\mu M_s,$$
$$\nu = 2,...,L-1, \tag{20a}$$

$$J_\nu = 2JS\sigma_\nu[\cos(\kappa_x/2)+\cos(\kappa_y/2)], \quad \nu = 1,2,...,L. \tag{20b}$$

The surface energy is, however, given by

$$E_1 = 4JS\sigma_1[1-\cos(\kappa_x/2)\cos(\kappa_y/2)] + 4JS\sigma_2 + D_s\Gamma_1 S\sigma_1 - 4\pi\mu M_s. \tag{20c}$$

The explicit calculation can be carried out layer by layer for a film of given thickness L. It can be shown[35] from Eqs. (11) and (16) that

$$\langle (S_\nu^z)^n S_\nu^- S_\nu^+ \rangle = \frac{1}{N^2}\sum_{\kappa,\alpha} \frac{U_{\nu\alpha}^2}{\exp(\omega_{\kappa\alpha}/k_BT)-1} \langle [S_\nu^+, (S_\nu^z)^n S_\nu^-] \rangle. \tag{21}$$

Then it follows, after some algebra with the spin operators, from Eq. (21) that

$$S(S+1)\langle (S_\nu^z)^n \rangle - \langle (S_\nu^z)^{n+1} \rangle - \langle (S_\nu^z)^{n+2} \rangle = R_\nu\{2\langle S_\nu^z (S_\nu^z-1)^n \rangle + \langle [(S_\nu^z-1)^n - (S_\nu^z)^n] \times [S(S+1) - S_\nu^z - (S_\nu^z)^2] \rangle\}, \tag{22a}$$

where we have defined

$$R_\nu=\frac{1}{(2\pi)^2}\int\int d\kappa_x\, d\kappa_y \sum_{\alpha=1}^{L}\frac{U_{\nu\alpha}^2}{e^{\omega_{\kappa\alpha}/k_BT}-1}. \quad (22b)$$

The reflection symmetry requires that $R_\nu=R_{L+1-\nu}$. Utilizing the relation[35] $\Pi_{m=-s}^{s}(S_\nu^z-m)=0$, we find from Eq. (22) the relative spontaneous magnetization for the ML labeled ν

$$\langle S_i^z\rangle=S\sigma_\nu=\frac{(S-R_\nu)(1+R_\nu)^{2S+1}+(1+S+R_\nu)R_\nu^{2S+1}}{(1+R_\nu)^{2S+1}-R_\nu^{2S+1}}. \quad (23)$$

Through Eq. (22b), we can calculate from Eq. (23) the temperature dependence of the relative spontaneous magnetization $\sigma_\nu(T)$ as well as the Curie temperature $T_C(L)$ for a given film.

For bulk fcc ferromagnets, the Curie temperature is

$$T_C(\text{bulk})=\frac{4S(S+1)}{C}\frac{J}{k_B},$$

with $C=1.344\,66$. In the following numerical computation, we fix the coupling constant $J=14.483$ meV by setting $T_C(\text{bulk})=1000$ K for bulk fcc iron. Other relevant parameters for fcc iron films are $S=1$, $\mu=2.2\mu_B$, $a=3.60$ Å, and $M_s(0)=1749$ G.

The relative spontaneous magnetization $\sigma_\nu(T)$ is calculated for each ML in films of various thickness. In Fig. 1, we plot σ_ν versus the reduced temperature for a film of (a) $L=4$, (b) $L=7$ and $D_s=1.1$ meV. It is seen that, for a fixed temperature, the relative spontaneous magnetization of an ML increases from the surface to interior. For example, $\sigma_1<\sigma_2<\sigma_3<\sigma_4$ in Fig. 1(b). On the other hand, σ_ν decreases with increasing temperature for a given monolayer. The strong reduction of the surface magnetization as compared to the inner layers has been observed and identified as the origin of the reorientation transition in the past.[17,18,24] Our calculation actually shows that there are two types of phase transition. For the film with $L=4$, σ_ν decreases to zero as the temperature increases to T_C, the system transforms from ferromagnetism to paramagnetism. For the film with $L=7$, σ_ν decreases monotonically as T increases, but suddenly vanishes at a transition temperature T_R at which the magnetization changes its direction from perpendicular to in plane. This is because the energy gap at the bottom of spin-wave spectrum becomes zero. We shall come back to this point in the next section.

IV. TEMPERATURE-DEPENDENT ANISOTROPY AND THE TRANSITION TEMPERATURE

To study the perpendicular anisotropy in magnetic films, it is more convenient to choose the (XYZ) coordinates with Z axis parallel to the spontaneous magnetization. The angle between Z- and z-axis is denoted by θ. The spatial coordinate x, y, and z axes represent the crystal plane orientation [100], [010], and [001], respectively. In the XYZ frame, the Hamiltonian is obtained from Eq. (1) by a transformation[35] and the result takes the form

$$\begin{aligned}H=&-\tfrac{1}{2}\sum_{\langle ij\rangle}J_{ij}[S_i^ZS_j^Z+\tfrac{1}{2}(S_i^+S_j^-+S_i^-S_j^+)]\\&-\sum_i D_i\Big\{\cos^2\theta(S_i^Z)^2+\tfrac{1}{4}\sin^2\theta[(S_i^+)^2+(S_i^-)^2]\\&+\frac{1}{2}\sin\theta\cos\theta[S_i^Z(S_i^++S_i^-)+(S_i^++S_i^-)S_i^Z]+\tfrac{1}{4}\sin^2\theta(S_i^+S_i^-+S_i^-S_i^+)\Big\}\\&+\frac{\mu^2}{2V}N_z\sum_{ij}[\cos^2\theta S_i^ZS_j^Z+\tfrac{1}{2}\sin\theta\cos\theta(S_i^ZS_j^++S_i^ZS_j^-+S_i^+S_j^Z+S_i^-S_j^Z)\\&+\tfrac{1}{4}\sin^2\theta(S_i^+S_j^++S_i^+S_j^-+S_i^-S_j^++S_i^-S_j^-)],\end{aligned} \quad (24)$$

where, as usual, $S^\pm=S^X\pm iS^Y$. The free energy of the system can be written as

$$F=F_{\text{ex}}+F_k+F_d=-k_BT\ln\{\text{tr}[\exp(-H/k_BT)]\}, \quad (25a)$$

where F_{ex} is the exchange energy, F_k represents the crystalline anisotropy energy, and F_d stands for the demagnetization or shape anisotropy energy.

We now proceed to calculate the uniaxial anisotropy $K_u(T)$, the surface anisotropy $K_s(T)$, and the shape anisotropy $K_d(T)$ as functions of T and L. As is shown in the following, there exists a PR in films of a sizable range of thickness. We shall also show that for the reorientation transition between states in which the magnetization is perpendicular and parallel to the film surface, the transition temperature T_R depends strongly on D_s.

In terms of the uniaxial anisotropy, the free energy F is given by

$$F/V=F_0/V+K_2\sin^2\theta+K_4\sin^4\theta+\cdots. \quad (25b)$$

The anisotropy coefficients depend in general on the temperature and the film thickness. The direction of magnetization is determined by the sign of K_2. It is in plane if $K_2<0$ and out of plane if $K_2>0$. Let us define $K_u(T)=K_2$ in Eq. (25b), then we have

$$K_u(T)=\frac{1}{V}\frac{\partial F}{\partial(\sin^2\theta)}=-\frac{1}{V}\frac{\partial F}{\partial(\cos^2\theta)}$$
$$=-\frac{1}{V}\mathrm{tr}\left[\frac{\partial H}{\partial(\cos^2\theta)}e^{-H/k_BT}\right]\Big/\ \mathrm{tr}(e^{-H/k_BT})$$
$$=-\frac{1}{V}\left\langle\frac{\partial H}{\partial(\cos^2\theta)}\right\rangle$$
$$=K(T)-K_d(T), \tag{26a}$$

$$K(T)=\frac{2N^2}{V}\sum_\nu\frac{D_\nu}{2}[3\langle(S_\nu^Z)^2\rangle-S(S+1)]$$
$$=\frac{N^2}{V}\sum_\nu D_\nu\Gamma_\nu\langle S_\nu^Z\rangle^2$$
$$=\frac{N^2}{V}\sum_{\nu=1,L}D_\nu\Gamma_\nu\langle S_\nu^Z\rangle^2+\frac{N^2}{V}\sum_{\nu=2}^{L-1}D_\nu\Gamma_\nu\langle S_\nu^Z\rangle^2$$
$$=\frac{2K_s(T)}{d}+K_v(T), \tag{26b}$$

$$K_d(T)=2\pi\left(\mu\sum_\nu\langle S_\nu^Z\rangle\Big/Lv\right)^2=2\pi[M_s(T)]^2, \tag{26c}$$

where we have defined the film thickness $d=La/2$. It is noted that the statistical mean of spin operators are already evaluated in Eqs. (26). Since the quantization axis is Z axis, it is clear that $\langle S_i^X\rangle=\langle S_i^Y\rangle=0$ and $\langle S_i^\pm\rangle=0$. In the derivation of Eq. (26b), we have also made use of the relation $\langle(S_i^Z)^2\rangle=S(S+1)-(1+2R_\nu)\langle S_i^Z\rangle$, which follows directly from Eq. (22a) by setting $n=0$. The anisotropy K in Eq. (26a) has been split into two parts for convenience, the surface anisotropy

$$K_s=\frac{N^2}{V}\frac{d}{2}\sum_{\nu=1,L}D_\nu\Gamma_\nu\langle S_\nu^Z\rangle^2$$

and the volume anisotropy

$$K_v=\frac{N^2}{V}\sum_{\nu=2}^{L-1}D_\nu\Gamma_\nu\langle S_\nu^Z\rangle^2$$

for interior ML. In the case of Fe films, we assume that $D_1=D_L=D_s$ for surfaces and $D_\nu=0$ for interior ML. Thus $K_v(T)=0$ and we have, in what follows,

$$K(T)=\frac{2}{d}K_s(T). \tag{27}$$

In general, the interior anisotropy does not vanish. An example is Ni films, for which the reorientation transition will be treated separately.[37]

For a ferromagnetic fcc Fe film, the surface anisotropy is given by

$$K_s(T)=\frac{2D_s}{a^2}[S(S+1)-\tfrac{3}{2}(1+2R_1)\langle S_1^Z\rangle]. \tag{28}$$

At absolute zero, $\sigma_1=1$ and $R_1=0$, we have

$$K_s(0)=\frac{2D_s}{a^2}S[S-\tfrac{1}{2}]. \tag{29}$$

When the temperature approaches T_C from below, $\sigma_\nu\to0$ and $R_\nu\to\infty$, and Eq. (23) becomes

$$3R_\nu\sigma_\nu=(S+1)-\frac{3}{2}\sigma_\nu-\frac{3(2S+3)(2S-1)}{20(S+1)}\sigma_\nu^2+O(\sigma_\nu^3). \tag{30}$$

Inserting Eq. (30) into Eq. (28), we find

$$K_s(T)=\frac{2D_s}{a^2}\left[\frac{3S(S+\frac{3}{2})(S-\frac{1}{2})}{5(S+1)}\sigma_1^2+O(\sigma_1^3)\right]. \tag{31}$$

The shape anisotropy is given by Eq. (26c), where the spontaneous magnetization is related to the absolute saturated magnetization by

$$K_d(T)=2\pi\left[M_s(0)\sum_{\nu=1}^{L}\sigma_\nu/L\right]^2. \tag{32}$$

We are now in a position to determine the transition temperature at which the perpendicular magnetization changes to in plane. This is achieved by considering the stability conditions for the PR. When the uniaxial anisotropy vanishes, the surface anisotropy and demagnetization (shape anisotropy) energies balance. Thus we have the condition $K_u(T_R)=0$ to determine the transition temperature T_R at which the RT between the perpendicular ($T<T_R$) and in-plane ($T>T_R$) orientations of the magnetization takes place. From the decoupling procedure introduced in Eqs. (13a)–(13c), it can be shown that the condition for $K_u(T_R)=0$ is equivalent to that for the zero energy gap at the bottom of the spin-wave spectrum.[37] If $K_u(T)>0$, the surface anisotropy is stronger than the shape anisotropy and a finite PR results. In general, $K_u(T)$ depends upon D_s, L, T, and $M_s(0)$. As long as $K_u(0)>0$, we find from Eqs. (26a), (27), (29), and (32) the relation

$$2D_s(S-1/2)/L-2\pi\mu M_s(0)>0, \tag{33}$$

which may then be regarded as the condition for a finite PR at absolute zero. Equation (33) implies that a stronger D_s, a smaller L, or a smaller $M_s(0)$ favors the existence of PR.

The temperature dependence of anisotropies is calculated for magnetic Fe films of 1–8 ML with the parameters $a=3.60$ Å and $M_s(0)=1749$ G. Our calculation indicates once more two types of transitions, similar to the magnetization. For $L\leqslant4$, all the anisotropies are at their maximum value at absolute zero and decrease with increasing temperature until the magnetization vanishes. Eventually, they become zero at the Curie temperature. The results for $L=4$ and $D_s=1.1$ meV are shown in Fig. 2(a). This is the transition from ferromagnetism to paramagnetism. For $L\geqslant5$, the reorientation transition from perpendicular to in plane takes place below T_C. This is illustrated in Fig. 2(b) in which the anisotropies are plotted versus the reduced temperature for $L=7$ and $D_s=1.1$ meV.

It is important to note that the curves in Fig. 2(b) do not mean that K, K_d, and K_s stop to exist beyond T_R until T_C. They simply indicate that we have only considered the nor-

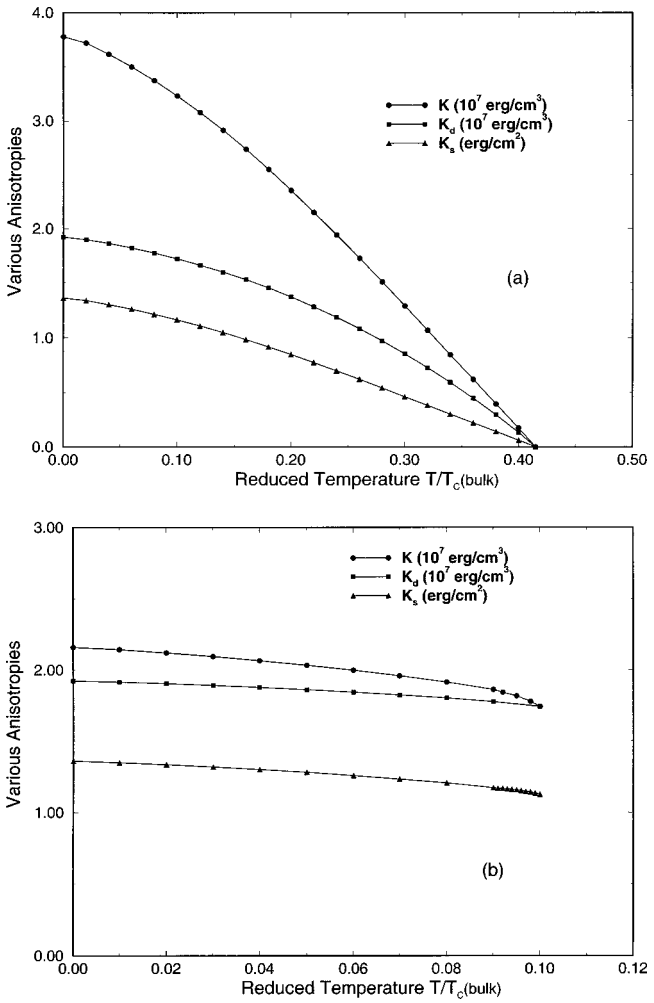

FIG. 2. Temperature dependence of various anisotropies for $D_s = 1.1$ meV. (a) $L = 4$ and (b) $L = 7$.

mal component of magnetization in the above calculation. The anisotropies are computed from Eqs. (26) up to the transition temperature T_R. In other words, we are assuming that the perpendicular component of magnetization vanishes at T_R and the in-plane component shows up at the same temperature. This is not exactly the case in experiments where the canted-spin phase has been observed, i.e., there is a very small temperature range around T_R, in which both the perpendicular and in-plane components are nonvanishing.[2,5,7]

When D_s is smaller than a critical value D_s^c, the spontaneous magnetization of the surfaces is smaller than that in interior monolayers, namely, σ_1, $\sigma_L < \sigma_\nu$, where $1 < \nu < L$. Further, σ_1 and σ_L decrease more rapidly than σ_ν for all $1 < \nu < L$ when the temperature increases. It is seen from the figure that $K(T)$ drops faster than $K_d(T)$ and eventually they meet at T_R, where all σ's drop to zero abruptly. Thus the condition for reorientation transition is

$$K_u(T_R) = K(T_R) - K_d(T_R) = 0. \tag{34}$$

The transition temperature, as well as the Curie temperature calculated above for an fcc Fe film, is presented along with experimental data[2,8] in Fig. 3 as a function of L for the anisotropy coupling $D_s = 0.84$, 1.0, 1.1, and 1.2 meV. Solid symbols represent T_C and open symbols represent T_R. It is

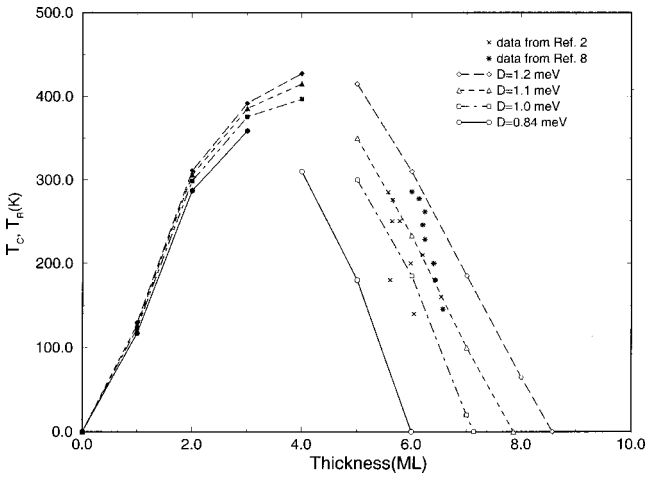

FIG. 3. Curie temperature T_C (solid symbols) and transition temperature T_R (open symbols) versus the film thickness for various D_s values. Experimental data for T_R are taken from Refs. 2 and 8.

interesting to observe that there exists a critical thickness L_c in a film of L monolayers and $L_c = 6$, 7.14, 7.86, and 8.57 corresponding to the above four D_s values, respectively. It should be remarked that we are not able to deal with films with a fraction of monolayers in the present theory. For a fixed D_s, we find that T_R increases with decreasing L as expected. Figure 3 illustrates that the experimental data can be accounted for by assuming a value of D_s between 1 and 1.2 meV, depending on experimental conditions. Finally, it is also interesting to mention that T_R and T_C curves form the boundary of a region in the TL plane in which the perpendicularly magnetized state of the film is stable. In other words, a finite PR may be observed within a certain range of temperature and thickness in a ferromagnetic film of specified D_s and $M_s(0)$.

V. DISCUSSION

By means of the Green-function technique, we have calculated from the Hamiltonian (1) the temperature dependence of perpendicular magnetization $\sigma_\nu(T)$ for every ML in a ferromagnetic fcc Fe film consisting of L ML. Various anisotropies are also obtained from this microscopic theory, but only the surface and shape anisotropies K_s and K_d are necessary for the Fe film. The Curie temperature determined by magnetization and the transition temperature obtained from anisotropy are then calculated as a function of L for several values of the anisotropic coupling D_s. It is particularly interesting to point out that the phase transitions are of different nature for films with $L \leqslant 4$ and $L > 4$. Our study of spontaneous magnetization and anisotropies both indicate that the ferromagnetism to paramagnetism transition occurs at T_C when $L \leqslant 4$, and reorientation transition appears at T_R when $L > 4$.

It is difficult to make quantitative comparison with the data, which depend sensitively on the sample preparation procedures in different experiments. However, our results presented in Fig. 3 can qualitatively account for various measurements. The PR stability region of 1.5–5.9 ML for 100-K growth reported in the study of the range of growth conditions that support PR (Ref. 1) may be described by assuming

$D_s = 0.84$ meV. The reorientation observed in Fe/Cu(100) films of 5–6.5 ML in the temperature range of 300–150 K (Ref. 2) suggests that the anisotropic coupling $D_s = 1$ meV. The transition is attributed to the temperature dependence of the surface uniaxial anisotropy in Ref. 2. The ultrathin fcc Fe/Cu(001) films are found to be ferromagnetic with $T_C = 230$ K for 1 ML, and 390 K for films of 3 and 5 ML.[3] The trend of variation is in agreement with our results in Fig. 3. The PR has also been observed below a critical thickness of about 5–6 ML for fcc Fe/Cu(100), Fe/Cu(110), and bcc Fe(110)/Cu(111) films.[4] The critical thickness can be slightly shifted for different samples by subtle changes in substrate perfection. For example, a deposition of homoepitaxial Cu film in the case of Fe/Cu(100) can extend L_c to ~7 ML, and, according to Fig. 3, a finite PR can exist in a film of 7 ML for $1 < D_s < 1.1$ meV. The termination of the vertical ferromagnetic phase in Ref. 8 may be explained by assuming $1.1 < D_s < 1.2$ meV.

In addition to the experiments mentioned above, it has also been discovered that magnetic films may exhibit very different properties under different procedures of sample preparation.[9] In their study of the interplay between magnetic and structural stabilities, Bader and co-workers have found that clean Fe/Cu(100) films at room temperature are ferromagnetic with a perpendicular easy axis if L is 2–4 ML, and become antiferromagnetic with ferromagnetic surfaces when L is 6–11 ML. However, it remains ferromagnetic and undergoes a spin-reorientation transition to in-plane at ~6 ML if the film is grown below 200 K and annealed to room temperature. The phenomena may be related to the variation of coupling constant J for intra-plane and interplane nearest neighbors in different monolayers. Studies of this subject are being carried out and will be reported in the future.

Aside from the reorientation phenomena observed in Fe films, an unusual change of direction of the magnetization from in plane to perpendicular with increasing temperature and film thickness has also been observed in ultrathin Ni films grown on Cu.[10–14] This is, however, not surprising. As a matter of fact, the temperature dependence of the second-order anisotropy calculated from the Hubbard model predicts both the reorientation transitions, the Fe type from out of plane to in plane and the Ni type from in plane to out of plane.[24] A similar conclusion is also obtained in a mean-field treatment,[17] in which another in-plane reorientation of magnetization may be found.

In addition to the two types of in-plane and out-of-plane transitions with increasing temperature and film thickness, a special transition in which the magnetization switches from perpendicular to in-plane direction with increasing temperature but decreasing thickness is also found experimentally[15] and theoretically.[16] The microscopic theory developed in this paper is capable to handle all in-plane and out-of-plane transitions by adjusting the anisotropy parameters D_ν. By assuming $D_\nu = 0$ for interior ML, our results presented here are in good agreement with the experimental data for Fe type. Since the volume anisotropy favors the out-of-plane orientation of the magnetization, it is expected that the Ni-type transition can also be accounted by a nonvanishing D_ν.

Finally, we recall that the canted-spin structures are observed in both Fe (Refs. 2, 5, and 7) and Ni (Refs. 11 and 38) films. Thus the reorientation transition may involve such canted-spin phases. Additionally, it is also interesting to point out that the reorientation transition is in general not necessarily confined to a single plane normal to the surface.[11,38] Although we have not touched this subject so far, we believe that the microscopic theory developed here is capable to handle both the perpendicular and in-plane components of magnetization in our study of Ni films. Work along these lines is being undertaken and will be reported elsewhere.[37]

ACKNOWLEDGMENT

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[1] C. Liu, E. R. Moog, and S. D. Bader, Phys. Rev. Lett. **60**, 2422 (1988); J. Appl. Phys. **64**, 5325 (1988).
[2] D. P. Pappas, K. P. Kamper, and H. Hopster, Phys. Rev. Lett. **64**, 3179 (1990); D. P. Pappas, K. P. Kamper, B. P. Miller, and H. Hopster, J. Appl. Phys. **69**, 5209 (1991).
[3] D. Pescia, M. Stampanoni, G. L. Bona, A. Vaterlaus, R. F. Willis, and F. Meier, Phys. Rev. Lett. **58**, 2126 (1987).
[4] M. T. Kief and W. F. Egelhoff, Jr., J. Appl. Phys. **73**, 6195 (1993).
[5] R. Allenspach and A. Bischof, Phys. Rev. Lett. **69**, 3385 (1992).
[6] D. P. Papas, C. R. Brundle, and H. Hopster, Phys. Rev. B **45**, 8169 (1992).
[7] Z. Q. Qiu, J. Pearson, and S. D. Bader, Phys. Rev. Lett. **70**, 1006 (1993).
[8] S. D. Bader, Dongqi Li, and Z. Q. Qiu, J. Appl. Phys. **76**, 6419 (1994).
[9] D. Li, M. Freitag, J. Pearson, Z. Q. Qiu, and S. D. Bader, J. Appl. Phys. **76**, 6425 (1994).
[10] M. Farle, W. Platow, A. N. Anisimov, P. Poulopoulos, and K. Baberschke, Phys. Rev. B **56**, 5100 (1997).
[11] M. Farle, B. Mirwald-Schulz, A. N. Anisimov, W. Platow, and K. Baberschke, Phys. Rev. B **55**, 3708 (1997).
[12] W. L. O'Brien, T. Droubay, and B. P. Tonner, Phys. Rev. B **54**, 9297 (1996).
[13] B. Schulz and K. Baberschke, Phys. Rev. B **50**, 13 467 (1994).
[14] F. Huang, M. T. Kief, G. J. Mankey, and R. F. Wills, Phys. Rev. B **49**, 3962 (1994).
[15] H. Fritzsche, J. Kohlhepp, H. J. Elmers, and U. Gradmann, Phys. Rev. B **49**, 15 665 (1994).
[16] A. Hucht and K. D. Usadel, J. Magn. Magn. Mater. **203**, 88 (1999).
[17] P. J. Jensen and K. H. Bennemann, Phys. Rev. B **42**, 849 (1990); Solid State Commun. **100**, 585 (1996); **105**, 577 (1998).
[18] A. Hucht and K. D. Usadel, Phys. Rev. B **55**, 12 309 (1997).
[19] A. Moschel and K. D. Usadel, Phys. Rev. B **49**, 12 868 (1994); **51**, 16 111 (1995).
[20] D. Pescia and V. L. Pokrovsky, Phys. Rev. Lett. **65**, 2599 (1990); **70**, 1183 (1993).

[21] A. Hucht, A. Moschel, and K. D. Usadel, J. Magn. Magn. Mater. **148**, 32 (1995).
[22] R. P. Erickson and D. L. Mills, Phys. Rev. B **46**, 861 (1992).
[23] A. Kashuba and V. L. Pokrovsky, Phys. Rev. Lett. **70**, 3155 (1993).
[24] T. Hermann, M. Potthoff, and W. Nolting, Phys. Rev. B **58**, 831 (1998).
[25] S. T. Chui, Phys. Rev. Lett. **74**, 3896 (1995); Phys. Rev. B **50**, 12 559 (1994).
[26] Y. Millev and M. Fähnle, Phys. Rev. B **51**, 2937 (1995).
[27] Y. Millev and J. Kirschner, Phys. Rev. B **54**, 4137 (1996).
[28] R. Lorenz and J. Hafner, Phys. Rev. B **54**, 15 937 (1996).
[29] N. N. Bogolyubov and S. V. Tyablikov, Dokl. Akad. Nauk. SSSR **126**, 53 (1959) [Sov. Phys. Dokl. **4**, 589 (1959)].
[30] R. A. Tahir-Kheli and D. Ter Haar, Phys. Rev. **127**, 88 (1962); **127**, 95 (1962).
[31] H. B. Callen, Phys. Rev. **130**, 890 (1963).
[32] Fu-Cho Pu, Dokl. Akad. Nauk. SSSR **130**, 1244 (1960); [Sov. Phys. Dokl. **5**, 128 (1960)]; **131**, 546 (1960) [**5**, 321 (1960)].
[33] M. E. Lines, Phys. Rev. **135**, A1336 (1964).
[34] D. L. Lin and H. Zheng, Phys. Rev. B **37**, 5394 (1988); H. Zheng and D. L. Lin, *ibid.* **37**, 9615 (1988).
[35] S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum, New York, 1967), Secs. 5 and 35.
[36] N. A. Potapkob, Dokl. Akad. Nauk. SSSR **144**, 297 (1962) [Sov. Phys. Dokl. **7**, 400 (1962)].
[37] W. Guo, L. P. Shi, and D. L. Lin (unpublished).
[38] S. S. Dhesi, H. A. Durr, and G. van der Laan, Phys. Rev. B **59**, 8408 (1999).