Computer Simulation of Surface Phase Transitions of Antiferromagnetic Films

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Abstract. The article gives a research of surface phase transitions in thin films described by the Ising antiferromagnetic model by Monte Carlo computer simulation. The simulation is carried out at different values of exchange integrals proportion on the surface and in the bulk of the system. The difference between the exchange integral of interaction between the surface spins and the first subsurface layer from the bulk value is also taken into account. It is shown that the phase diagram of the system has a phase where the ordering of spins on the surface of the system occurs at temperatures below the Neel temperature. The difference between the temperatures of the surface phase transition from the temperature of the bulk phase transition is greater than in semi-infinite systems. This difference is explained by the lower influence of bulk ordering on surface ordering.

1. Introduction
Surface magnetism is observed experimentally in both ferromagnetic and antiferromagnetic systems. The term of surface magnetic energy [1] was introduced to describe this phenomenon. This term allowed us to calculate the shift of Curie temperature on the free surface of semi-infinite ferromagnetic systems to the bulk value.

Phase diagram of semi-infinite systems with free surface [2, 3] can be constructed on the basis of phenomenological approach. This phase diagram is shown in figure 1.

The system may have three phases associated with the ordering of surface and bulk spins: disordered phase (SD/BD), surface-ordered bulk-dis-ordered phase (SO/BD), surface-ordered bulk-ordered phase (SO/BO).
Figure 1. Phase diagram of semi-infinite systems with free surface constructed on the basis of phenomenological approach.

It can be concluded about the possibility of three types of phase transitions from the form of a phase diagram. SD/BD to SO/BD transition is referred to surface phase transition, SO/BD to SO/BO transition is referred to extraordinary phase transition, SD/BD to SO/BO transition is referred to ordinary or bulk phase transition. Three lines of phase transitions intersect at a tricritical point. Phase transition in this point named special phase transition. Critical phenomena near the lines of these transitions in the framework of the field-theoretical approach using $\varepsilon$-decomposition are described in [4], directly in three-dimensional space in the article [5], in systems with two order parameters in the work [6].

The excess of the surface phase transition temperature $T_S$ over the volume transition temperature $T_C$ was observed experimentally in a number of papers for polycrystalline Gd [7] ($T_S - T_C = 15$ K). However, there were experimentally observed cases in which surface ordering occurs at a lower temperature. For example, for antiferromagnetic macroscopic crystal Fe$_3$BO$_6$ $T_S - T_C = 8.5$ K, crystal Fe$_3$BO$_6$ [8] $T_S - T_C = 5$ K.

The difference between the value of surface and bulk exchange integrals was calculated from first principles in [9, 10], and confirmed experimentally [11, 12]. In article [13] it is shown that surface energy of FeO linearly depends on chemical potential on the basis of calculations from the first principles. In work [9] calculations from the first principles for Gd have shown that distance between atoms in volume of a crystal is equal to 3.52 Å, whereas on a surface 3.64 Å, that leads to difference in values of exchange integrals, respectively $J_S = 1.25$ and $J_B = 1.51$, and, therefore, their relation $R = J_S / J_B = 0.83$. Computer simulation of both ferromagnetic and antiferromagnetic semi-infinite systems [14, 15, 16] showed that the temperature of the surface phase transition exceeds the volume one when ratio of the surface exchange integral to the bulk exchange integral $J_S / J_B > 1.55$. It is observed the special phase transition when set to $J_S / J_B = 1.55$. In this case, the phase diagram coincides with the predicted phenomenological theory. The possibility of a state in which the volumetric temperature exceeds the surface temperature for the ferromagnetic Ising model was shown in articles [17, 18] by computer simulation methods. In this case, the phase diagram of the substance observed surface-disordered volume-ordered phase (SD/BO). The existence of such a phase is possible when

\[ R = \frac{J_S}{J_B} = 0.83 \]
The ratio of the exchange integrals $J_S/J_B<1$. The lines of phase transitions cross at two tricritical points (Fig. 2).

In computer simulation of critical behavior, it is assumed that the exchange interaction between spins on the surface differs in magnitude from the interaction in the system volume, both in semi-infinite systems and in films. The fact that the interaction between the surface spins and the first subsurface layer is also different from the volume one is not taken into account. However, taking into account this effect can significantly affect the phase diagram of the system and the regime of critical behavior, as far as the volume of the system and the surface in the ordering play for each other the role of an external field. The value of the exchange integral between the surface spins and the first subsurface layer determines the intensity of their interaction. As shown in [19] for semi-infinite antiferromagnets, taking into account this effect changes the phase diagram of the system. There is one tetracritical point on the phase diagram instead of two tricritical points.

The purpose of our article is research of the phase transitions in thin films described by the Ising antiferromagnetic model by computer simulation at different values of surface energy and the value of interaction between the surface and the subsurface layer.

2. Description of the system

Hamiltonian of semi-infinite antiferromagnetic Ising model may be written as:

$$H = -J_B \sum_{B} S_i S_j - J_S \sum_{S} S_i S_j - J_{SB} \sum_{BS} S_i S_j,$$

where $S_i$ is value of spin $i$ point ($\pm \frac{1}{2}$). Addition is carried out over nearest neighbours. The first sum includes all pairs of spins of the nearest neighbors located not on the surface of the film. In the second one pairs of nearest spins located on one of the surfaces are summed. In the third sum in each pair, one spin is located on one of the surfaces, and the second in the nearest subsurface layer. As already mentioned in the introduction, exchange integrals may differ, so we introduce two parameters $R_S = J_S/J_B$ and $R_{SB} = J_{SB}/J_B$.

In this paper, computer simulation was carried out by Monte Carlo method using the metropolis algorithm for thin films described by the antiferromagnetic Ising model with cubic lattice. The lattice had linear dimensions $L \times L \times D$, where $D$ is the film thickness. The free surface planes were defined by equations $z = 0$ and $z = D-1$. Periodic boundary conditions were used along the $OX$ and $OY$ axes. Theory of finite-dimensional scaling was used for determination phase transition temperature [15].
Let us introduce two order parameters to describe antiferromagnetic phase transitions. The order parameter \( m \) will determine the antiferromagnetic order in the main system volume and it is calculated as staggered magnetization of all system. It is equal to difference between magnetic moments of two sublattice. The order parameter \( m_S \) is introduced to investigate the surface phase transition. It is calculated as staggered magnetization of free-surface located spins.

Critical temperature of transition was defined by bulk and surface Binder’s quartic cumulants:

\[
U = 1 - \frac{\langle m^4 \rangle}{3\langle m^2 \rangle^2}, \quad U_S = 1 - \frac{\langle m_S^4 \rangle}{3\langle m_S^2 \rangle^2}.
\]

(2)

Angle brackets mean thermodynamic averaging.

Temperature of phase transition can be defined by the position of the intersection point of cumulants for systems with different sizes of \( L \). \( U \) cumulants were used to find the bulk critical temperature \( T_N \), the behavior of \( U_S \) cumulants was investigated to determine the temperature of the surface phase transition \( T_S \).

Fluctuation relations were used to calculate the bulk and the surface susceptibility:

\[
\chi = NK \left\langle \left( m^3 \right) - \left\langle m \right\rangle^2 \right\rangle,
\]

(3)

\[
\chi_S = SK \left\langle \left( m_S^3 \right) - \left\langle n_S \right\rangle^2 \right\rangle.
\]

(4)

\[
K = \frac{\sqrt{S}}{k_B T},
\]

(5)

\[
N = DL^2,
\]

(6)

\[
S = L^2.
\]

(7)

\( k_B \) – Boltzmann constant, (6) – number of system points, (7) – number of surface points. Angle brackets mean thermodynamic averaging.

Susceptibilities in the critical region satisfy the following relation:

\[
\chi \sim L^{\gamma/\nu},
\]

(8)

\[
\chi_S \sim L_S^{\gamma_S/\nu_S}.
\]

(9)

The proportion of the critical indexes \( \gamma/\nu \) and \( \gamma_S/\nu_S \) can be found from this ratio. The critical indexes \( \nu \) and \( \nu_S \) can be calculated from (10) and (11):

\[
\frac{dU}{dT} \sim L^{-1/\nu},
\]

(10)

\[
\frac{dU_S}{dT} \sim L^{-1/\nu_S}.
\]

(11)
Other critical indices can be found from scaling relations:

$$\eta_S = 2 - \frac{\gamma_S}{\nu_S},$$

(12)

$$\alpha_S = 2 - D\nu_S,$$

(13)

$$\beta_S = \frac{\nu_S}{2}(D - 2 + \eta_S).$$

(14)

## 3. Results of computer simulation

Computer experiment was carried out for antiferromagnetic films with thickness from $D = 4$ to $D = 16$. The value of the ratio of the exchange integrals $R = J_S / J_B$ ran from $R_S = 0.5$ to $R_S = 2.0$ in increments of 0.1. The extreme values $RSB = 1$ and $RSB = RS$ were taken for the second ratio of exchange integrals. The Neel temperature $T_N$ of the bulk transition and the surface phase transition temperature $T_S$ were calculated for all parameter values.

First of all, it should be noted that in thin films, the Neel temperature of bulk phase transition depends on the thickness of the film and of both relations of exchange integrals. This picture significantly differs from semi-infinite systems, where the Neel temperature of bulk phase transition does not depend on the ratio of exchange integrals and coincides with the corresponding value for unbounded systems. The dependence of the Neel temperature $T_N$ of the bulk phase transition on the ratio of exchange integrals $R_S$ at $RSB = 1$ for films of different thickness $D$ is shown in figure 3. Similar graphs for $RSB = RS$ are shown in figure 4.

![Figure 3](image_url)

**Figure 3.** The dependence of the Neel temperature $T_N$ of the bulk phase transition on the ratio of exchange integrals $R_S$ at $RSB = 1$ for films of different thickness $D$. 
Figure 4. The dependence of the Neel temperature $T_N$ of the bulk phase transition on the ratio of exchange integrals $R_S$ at $R_{SB} = R_S$ for films of different thickness $D$.

As can be seen from figures 3 and 4, the temperature of the bulk phase transition increases with the increase of $R_S$. This dependence is easily explained by the influence of surface energy on the whole system. This effect is absent in a semi-infinite system because the surface gives an infinitely small contribution to the energy of the system. For thin films, two surface layers make up a significant part of the system and have a great influence on the behavior of its thermodynamic functions. A similar dependence was obtained for ferromagnetic thin films in [20]. The comparison of figures 3 and 4 shows that the difference the exchange integral of the interaction of the surface layer from the first subsurface layer leads to a faster increase in the temperature of the phase transition.

The SD/OB phase for thin films is not observed. The effect of the surface layer of the spins on the whole system is great, so there is one transition with an intermediate temperature instead of two independent transitions. For thin films, the tricritical point to the right of which there is a surface phase transition is characterized by high temperature and high values of the ratio of $R_S$ exchange integrals, which cannot be observed in real systems. For example, for $D = 6$ the tricritical point is observed at $R_S = 3.1$.

4. Conclusion

Thus, the critical behavior of thin antiferromagnetic films differs from that of semi-infinite systems. First of all, the temperature of the bulk phase transition is not constant, but increases with increasing surface energy. A surface phase transition can be observed only by large relations of exchange integrals lying in the nonphysical region.

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