Surface magnetic properties of the Ising model with a diluted free surface

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A semi-infinite ferromagnetic simple cubic Ising lattice which has nonmagnetic impurities substituted for the magnetic species only at the surface is investigated with the use of a new type of effective-field theory with correlation. The surface magnetism is examined as a function of modified exchange $J_s = J(1+\Delta)$ and concentration P of magnetic atoms at the surface. The critical value Δ_c, transition temperatures T_c^s, and phase diagram for surface ordering are obtained as functions of P and Δ. The reduced magnetization curves of surface and bulk are also studied. We obtain some characteristic behaviors of magnetism at the diluted surface.

I. INTRODUCTION

The problems of surface magnetism have been investigated for many years. Among them the effects of surfaces on phase transitions have received much attention and have been studied by using a variety of approximations and mathematical techniques.[1-6] In the early stage of these investigations Mills[1] assumed a model in which the spins in the free surface interact among one another with an exchange parameter J_s which is different from the bulk exchange J. For this simple model with modified exchange only at the surface, it was pointed out on the basis of the traditional mean-field approximation (MFA) that for J_s greater than a critical value J_{sc}, the system would order on the surface before it ordered in the bulk. This MFA prediction is found to be qualitatively correct and quantitative improvement on the critical value $J_{sc}^{\mathrm{MFA}} = 1.25J$ have been obtained by using sophisticated techniques.[3-5]

On the other hand, in the previous works[7-9] some of the present authors have shown that a simple effective-field theory with correlation developed by Kaneyoshi *et al.*[10] leads to quite satisfactory results for surface magnetism. In fact, the critical value $\Delta_c = J_{sc}/J - 1$ was obtained to be 0.3068 which is in excellent agreement with the renormalization-group (RG) approach result ($\Delta_c^{\mathrm{RG}} = 0.307$) as reported in Ref. 5. The qualitative shortcoming of the MFA theory occurring when the exchange coupling between the surface and the second layer is allowed to be different from the bulk exchange parameter[5] was also removed by the simple theory.

Now, the theory of surface with a disordered magnetic composition seems to be far from complete, although some progress has been noted recently.[11-13] In particular, it is interesting both theoretically and experimentally to ask whether a system with magnetic atoms randomly distributed only at the surface can exhibit surface magnetism in the Mills's sense. This model may have experimental relevances with an amorphous magnetic layer deposited on a ferromagnetic crystalline system and ferromagnetic materials in which surface dilution can be produced artificially, e.g., by coating or ion implantation.

The subject of cooperative behavior of surface has obvious relations to various regions of condensed matters, so that even simple ideas like mean-field approximation have been discovered again and again. In this work, surface magnetic properties of the Ising model with magnetic atoms randomly distributed only at the surface are studied by using the simple effective-field theory with correlation. The critical value Δ_c is then obtained as a function of concentration P of surface magnetic atoms. In the pure surface with $P=1$, as mentioned above, the critical value Δ_c is given by $\Delta_c = 0.3068$. The transition temperatures for surface ordering are investigated as functions of P and $\Delta = J_s/J - 1$. We are also able to obtain the phase diagram characterizing the state of the magnetic surface as a function of P.

The outline of our paper is as follows. In Sec. II, we briefly review the basic points of the simple effective-field theory with correlation, when it is applied to the problem of a diluted surface. In Sec. III, we examine the phase diagram and the transition temperatures as functions of P and Δ. In Sec. IV, in order to compare the magnetic properties of diluted surface states with those of the purely two-dimensional diluted ferromagnet, within the formalism the diluted square lattice is investigated. Some interesting behaviors of normalized magnetization are found. In Sec. V, the reduced magnetization curves of surface and bulk are examined for two cases, namely $\Delta > \Delta_c(P=1)$ and $\Delta < \Delta_c(P=1)$. The reduced surface magnetization curves, when the concentration P of surface magnetic atoms is changed, are obtained for each case. In this work, we obtain some characteristic behaviors of magnetization at the diluted surface.

II. THEORY

We consider a model system, which is described by the Hamiltonian with nearest-neighbor interaction J in the

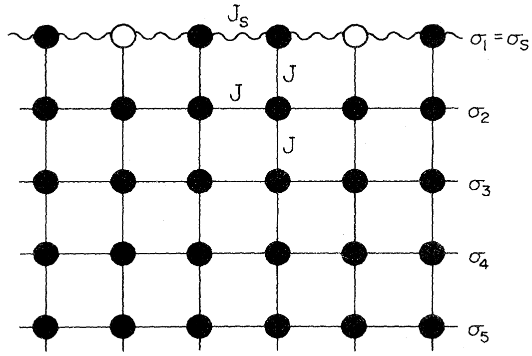

FIG. 1. Part of a two-dimensional cross section through a semi-infinite Ising lattice. Black points denote lattice positions, which are occupied by spins $\mu_i = \pm 1$. White points are nonmagnetic atoms. Full lines indicate exchange coupling J, while wavy lines indicate surface exchange couplings $J_s = (1+\Delta)$.

bulk of a simple cubic lattice, while the corresponding interaction in the surface place is J_s and magnetic atoms on the surface are randomly distributed (Fig. 1 shows a two-dimensional cross section of this system),

$$\mathscr{H} = -\tfrac{1}{2} \sum_{i,j} J_{ij} \mu_i \mu_j \; , \tag{1}$$

where $\mu_i = \pm 1$ is the usual Ising variable, and J_{ij} is the exchange interaction between spins at sites i and j, which takes the value J_s if both occupied spins lie on the surface, and the bulk value J otherwise.

Formal identities for the correlation functions of the Ising model have appeared in the literature for some time.[14] The starting point for the statistics of our spin system is the exact relation due to Callen[15]

$$\langle \mu_i \rangle = \left\langle \tanh \left[\beta \sum_j J_{ij} \mu_j \right] \right\rangle , \tag{2}$$

where the angular bracket indicates the usual ensemble average

$$\langle \cdots \rangle = \mathrm{Tr}[\, \exp(-\beta \mathscr{H}) \cdots] / \mathrm{Tr} \exp(-\beta \mathscr{H}) \; ,$$

and $\beta = (k_B T)^{-1}$. Here, in order to write the identity (2) in a form which is particularly amenable to approximation, let us introduce the differential operator technique proposed by Honmura and Kaneyoshi as follows:

$$\begin{aligned} \sigma_i \equiv \langle \mu_i \rangle &= \left\langle \exp \left[D \sum_j t_{ij} \mu_j \right] \right\rangle \tanh x \,|_{x=0} \\ &= \left\langle \prod_j [\, \cosh(D t_{ij}) + \mu_j \sinh(D t_{ij})] \right\rangle \tanh x \,|_{x=0} \; , \end{aligned} \tag{3}$$

where $D = \partial / \partial x$ is a differential operator, $t_{ij} = \beta J_{ij}$, and σ_i means the magnetization of an atom lying in the ith layer.

By assuming the statistical independence of lattice site, namely

$$\langle \mu_i \mu_j \cdots \mu_l \rangle \cong \langle \mu_i \rangle \langle \mu_j \rangle \cdots \langle \mu_l \rangle \; ,$$

Eq. (3) may be rewritten as

$$\sigma_i = \prod_\delta [\, \cosh(D t_{i,i+\delta}) + \sigma_{i+\delta} \sinh(D t_{i,i+\delta})] \tanh x \,|_{x=0} \; , \tag{4}$$

where δ only takes nearest neighbors of a site in the ith layer. The approximation led, in spite of its simplicity, to quite satisfactory results. In fact, the approximation essentially corresponds to the Zernike approximation[16] in the bulk problem, as will be also shown in Sec. V. The formalism has been applied to disordered magnetic systems, such as spin-glasses,[17] dilute and amorphous ferromagnets,[10,18] and systems with competing interactions.[19] As discussed in Refs. 8 and 9, when it was applied to the pure surface problem, the critical value Δ_c was obtained to be 0.3068, which is in excellent agreement with the RG result ($\Delta_c^{\mathrm{RG}} = 0.307$) as reported in Ref. 5. Phase diagrams, magnetization curves, susceptibilities, and specific heats of surface and bulk were successfully obtained by means of the approximation. In this work some of them will be rederived, in order to complete our understanding.

In the present system the magnetic atoms are randomly distributed on the surface. In order to take account of the fact explicitly, Eq. (4) can be also represented as

$$\sigma_i = \prod_\delta \{ \xi_{i+\delta} [\, \cosh(D t_{i,i+\delta}) + \sigma_{i+\delta} \sinh(D t_{i,i+\delta})] + (1 - \xi_{i+\delta}) \} \tanh x \,|_{x=0} \; , \tag{5}$$

where $\xi_{i+\delta}$ is a random variable which takes a value 1 or 0 depending on whether or not a magnetic atom on the surface is occupied, and otherwise must take the value of unity.[20]

Now, let us apply Eq. (5) to our layered simple cubic system with a diluted (1,0,0) surface. Performing the random average $\langle \cdots \rangle_r$ and noting that $\langle \xi_i \rangle_r = P$, for the surface magnetization σ_1, Eq. (5) yields

$$\begin{aligned} \sigma_1 = \{ & P[\cosh(D t_s) + \sigma_1 \sinh(D t_s)] + (1-P) \}^4 \\ & \times [\cosh(D t) + \sigma_2 \sinh(D t)] \tanh x \,|_{x=0} \; , \end{aligned} \tag{6}$$

where $t_s = J_s / k_B T$ and $t = J / k_B T$. For the magnetization σ_2 of the second layer we have

$$\begin{aligned} \sigma_2 = \{ & P[\cosh(D t) + \sigma_1 \sinh(D t)] + (1-P) \} \\ & \times [\cosh(D t) + \sigma_2 \sinh(D t)]^4 \\ & \times [\cosh(D t) + \sigma_3 \sinh(D t)] \tanh x \,|_{x=0} \; . \end{aligned} \tag{7}$$

In general, the magnetization σ_n of the nth layer is given by

$$\sigma_n = [\cosh(D t) + \sigma_n \sinh(D t)]^4 [\cosh(D t) + \sigma_{n-1} \sinh(D t)][\cosh(D t) + \sigma_{n+1} \sinh(D t)] \tanh x \,|_{x=0} \; , \quad n \geq 3 \tag{8}$$

where σ_{n-1} and σ_{n+1} are the magnetizations in the $(n-1)$th and $(n+1)$th layers, respectively.

In the following sections, we use Eq. (6)—(8) to examine the phase diagrams characterizing the state of the magnetic surface, transition temperatures of surface and bulk, and the temperature dependences of surface or bulk magnetization.

III. TRANSITION TEMPERATURES AND PHASE DIAGRAM

In this section we are concerned with the calculations of the critical temperature and the critical value Δ_c for surface ordering as functions of P and Δ. The usual argument that σ_i tends to zero as the temperature approaches a critical temperature allows us to consider only terms linear in σ_i, because higher order terms tend to zero faster than σ_i on approaching a critical temperature. Near the critical points, therefore, we can linearize Eqs. (6)—(8) and we find

$$\sigma_1=P^4(4A_1\sigma_1+A_2\sigma_2)+4P^3(1-P)(3A_3\sigma_1+A_4\sigma_2)+6P^2(1-P)^2(2A_5\sigma_1+A_6\sigma_2)$$
$$+4P(1-P)^3(A_7\sigma_1+A_8\sigma_2)+(1-P)^4A_9\sigma_2\ , \tag{9}$$

$$\sigma_2=PB_1(4\sigma_2+\sigma_1+\sigma_3)+(1-P)B_2(4\sigma_2+\sigma_3)\ , \tag{10}$$

and

$$\sigma_n=C(\sigma_{n-1}+4\sigma_n+\sigma_{n-1})\ ,\quad n\geq 3 \tag{11}$$

where the coefficients A_ν ($\nu=1,2,\ldots,9$), B_ν($\nu=1,2$), and C are given in Appendix. By applying a mathematical relation, i.e., $e^{\alpha D}f(x)=f(x+\alpha)$, all the coefficients can be expressed as a sum of transcendental functions $\tanh X$ with an appropriate argument X. For instance, the coefficient A_1 is given by

$$A_1=\cosh^3(Dt_s)\sinh(Dt_s)\cosh(Dt)\tanh x\,|_{x=0}$$
$$=\tfrac{1}{16}[\tanh(1+4\eta)t+2\tanh(1+2\eta)t$$
$$-2\tanh(1-2\eta)t-\tanh(1-4\eta)t]\ ,$$

where $\eta=J_s/J=1+\Delta$.

According to Ref. 3, let us assume that $\sigma_{n+1}=a\sigma_n$ for $n\geq 2$, e.g., the magnetization σ_n of each layer with n larger than $n=2$ decreases exponentially into the bulk. Equations (9) and (10) then yield the following secular equation:

$$\tilde{M}\begin{bmatrix}\sigma_1\\ \sigma_2\end{bmatrix}\equiv\begin{bmatrix}D_1,D_2\\ D_3,D_4\end{bmatrix}\begin{bmatrix}\sigma_1\\ \sigma_2\end{bmatrix}=0\ , \tag{12}$$

with

$$\begin{aligned}D_1&=4P^4A_1+12P^3(1-P)A_3+12P^2(1-P)^2A_5\\&\quad+4P(1-P)^2A_7-1\ ,\\ D_2&=P^4A_2+4P^3(1-P)A_4+6P^2(1-P)^2A_6\\&\quad+4P(1-P)^3A_8+(1-P)^4A_9\ ,\\ D_3&=PB_1\ ,\\ D_4&=4PB_1+4(1-P)B_2+a[PB_1+(1-P)B_2]-1\ .\end{aligned} \tag{13}$$

The parameter a is given by, upon using (11),

$$a=\frac{(1-4C)-[(1-4C)^2-4C^2]^{1/2}}{2C}\ . \tag{14}$$

Thus, the critical ferromagnetic frontiers can be derived from the condition $\det\tilde{M}=0$, namely

$$D_1D_4-D_2D_3=0\ . \tag{15}$$

From the formal solutions of Eq. (15) we choose those corresponding to the highest possible transition temperature T_c^s which is the temperature for surface ordering. In our present treatment the bulk transition temperature T_c^b can be determined by putting $\sigma_n=\sigma_{n-1}=\sigma_{n+1}=\sigma$ into Eq. (11), which is given by

$$t_c^b=\frac{J}{k_BT_c^b}=0.197$$

(see also Sec. V). This is an improvement on the traditional MFA, which provides $t_c^{\mathrm{MFA}}=0.167$.

In the previous work with a pure free surface[8] the critical value Δ_c for surface ordering was found to be 0.3068, compared to the mean-field value of 0.25. For $\Delta>\Delta_c$ there is a temperature region in which the surface behaves like a bulk two-dimensional Ising model near its phase transition, and for $\Delta<\Delta_c$ the surface only orders when the bulk does. The previous result of $\Delta_c=0.3068$ can be easily derived in this work on assuming $\sigma_1=\sigma_2=\sigma$ in Eq. (9) and putting $P=1$ and $t_c^b=0.1971$. In order to clarify the results of present work, in Fig. 2 we show again the phase diagram characterizing the state of the pure magnetic surface, which was obtained in Ref. 8 and is also derived from Eq. (15) on putting $P=1$. In the figure, we denote the paramagnetic, bulk-ferromagnetic, and surface-ferromagnetic phases by PM, BF, and SF, respectively, and SB denotes the multicritical point of the surface-bulk transition. The critical value $\Delta_c=0.3068$ is in excellent agreement with the result obtained by Burkhardt and

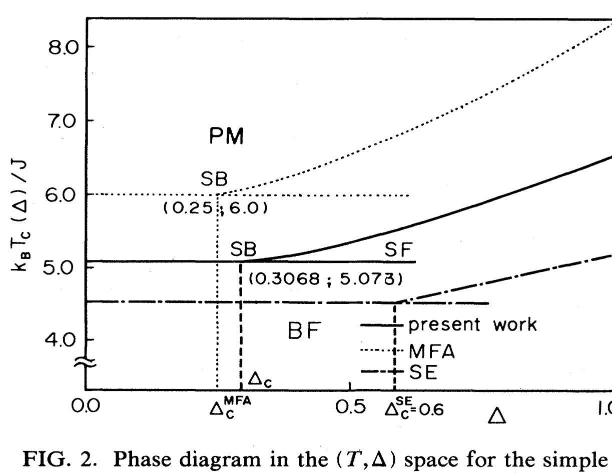

FIG. 2. Phase diagram in the (T,Δ) space for the simple cubic Ising model with $P=1$ and enhanced surface coupling $J_s=J(1+\Delta)$. For comparison, the MFA and SE results (Refs. 1 and 3) are also plotted as a function of Δ. The paramagnetic, bulk-ferromagnetic, and surface-ferromagnetic phases are indicated by PM, BF, and SF, respectively.

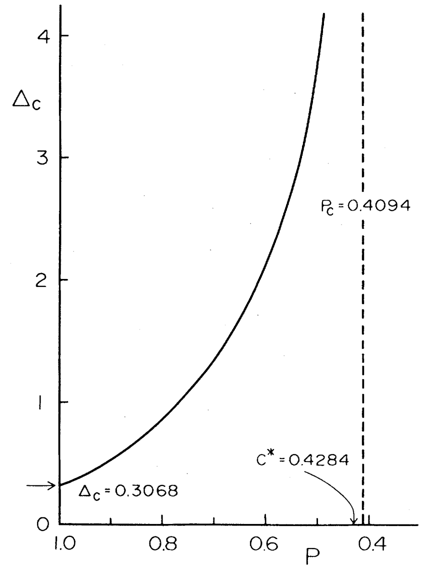

FIG. 3. Critical value Δ_c for surface ordering is plotted as a function of concentration P of magnetic atoms at the surface.

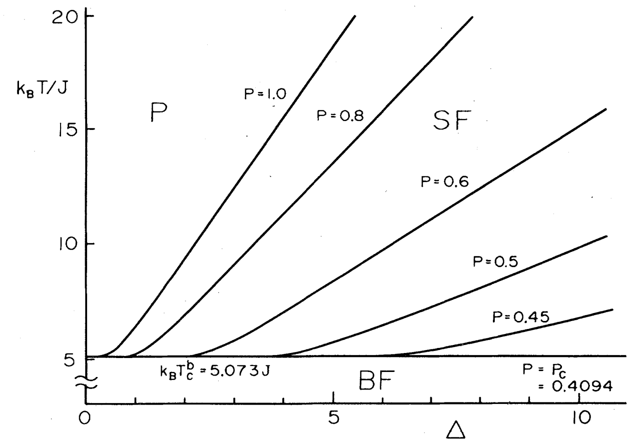

FIG. 5. Phase diagrams in the (T,Δ) space, when the concentration P of magnetic atoms at the surface is changed.

Eisenriegler[5] by using an RG approach within their first-order cumulant approximation $(\Delta_c^{RG}=0.307)$. For very large Δ, $T_c(\Delta)$ becomes asymptotic to the two-dimensional transition temperature $3.0898(1+\Delta)$. For comparison the results obtained from MFA and high-temperature series expansion (SE) method are also plotted.

Now, we are in a position to examine the effects of magnetic atoms randomly distributed at the surface on the critical value Δ_c, transition temperatures, and phase diagram. The effects can be obtained by solving Eq. (15) numerically. In Fig. 3 the critical value Δ_c for surface ordering is shown as a function of concentration P of magnetic atoms on the surface. The Δ_c starts at the value of 0.3068 for $P=1$ and then rapidly increases, when the concentration of magnetic atoms decreases. At the critical value of P given by $P_c=0.4094$ the Δ_c diverges to infinite. In other words it implies that the surface magnetism is impossible below the P_c in the Mills's sense. In relation to the result it is worth noting that, as will be discussed in the next section, the usual critical percolation concentration C^* in a dilute ferromagnetic Ising square lattice is within the present formalism given by $C^*=0.4284$, e.g., $T_c(C)=0$ at $C=C^*=0.4284$. Thus, it is an interesting problem whether or not the surface magnetism exists at the range of concentration between C^* and P_c. In a case[13] there exists the surface magnetism even below the bulk critical concentration C_B^*.

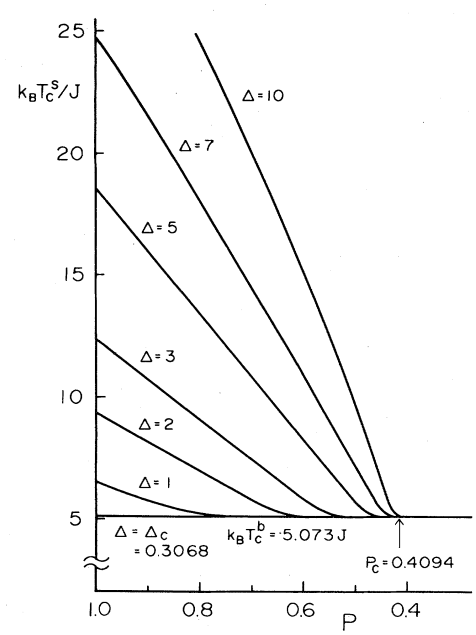

FIG. 4. Transition temperatures T_c^s for surface ordering are plotted as a function of surface concentration P. The values Δ taken are larger than the critical value Δ_c.

For $\Delta > \Delta_c$, the surface orders at a temperature T_c^s which is higher than the bulk T_c^b. In Fig. 4 the transition temperatures, T_c^s for surface ordering are depicted for some cases with $\Delta > \Delta_c$ as a function of concentration P of magnetic atoms at the surface. A characteristic behavior of the result is that near the T_c^b the curves of T_c^s have all downward curvatures, in comparison with the usual $T_c(C)$ curve in the dilution problem, which has an upward curvature near the critical concentration C_B^* (see the next section and Ref. 21). Another characteristic is that the curves, as a function of P, at first show weak downward curvature for small Δ and then change to weak upward curvature on increasing Δ, in contrast to the result (Fig. 6) of a dilute ferromagnetic changing linearly with C.

In Fig. 5, phase diagrams with enhanced surface coupling $J_s=J(1+\Delta)$ are depicted for some cases of surface concentration P. The phase diagram for $P=1$ is the same as that of Ref. 8 (or Fig. 2). Decreasing the surface concentration P, the surface ferromagnetic phase can be obtained only for cases with large values of Δ, in accordance with the result of Fig. 3.

IV. A DILUTE FERROMAGNETIC SQUARE LATTICE

As discussed in the preceding section, it will be worthwhile to examine a two-dimensional dilute ferromagnet within the present approximation, in order to compare the magnetic behaviors of the diluted surface with those of such a system in which magnetic atoms are randomly distributed on a square lattice. The magnetization σ of such a two-dimensional dilute ferromagnet is easily derived from Eq. (6), on putting $J=0$ (or $t=0$) into Eq. (6) as follows:

$$\sigma=\{C[\cosh(Dt_0)+\sigma\sinh(Dt_0)]+(1-C)\}^4\tanh x\,|_{x=0}\ , \tag{16}$$

with

$$t_0=\frac{J_0}{k_BT}\ ,$$

where J_0 and $C=\langle\xi_i\rangle_r$ are the exchange coupling for nearest neighbors and the concentration of magnetic atoms, respectively. We here changed the notations, in order to avoid the confusion between surface and bulk problems. Expanding Eq. (16), the magnetization σ is given by

$$\sigma=C^4(4\sigma K_1+4\sigma^3K_2)+4C^3(1-C)(3\sigma K_3+\sigma^3K_4)+12C^2(1-C)^2\sigma K_5+4C(1-C)^3\sigma K_6\ , \tag{17}$$

with

$$K_1=\sinh(Dt_0)\cosh^3(Dt_0)\tanh x\,|_{x=0}\ ,$$
$$K_2=\sinh^3(Dt_0)\cosh(Dt_0)\tanh x\,|_{x=0}\ ,$$
$$K_3=\sinh(Dt_0)\cosh^2(Dt_0)\tanh x\,|_{x=0}\ ,$$
$$K_4=\sinh^3(Dt_0)\tanh x\,|_{x=0}\ ,$$
$$K_5=\cosh(Dt_0)\sinh(Dt_0)\tanh x\,|_{x=0}\ ,$$
$$K_6=\sinh(Dt_0)\tanh x\,|_{x=0}\ ,$$

where the coefficients K_μ ($\mu=1-6$) can be also evaluated in terms of a mathematical relation $e^{\alpha D}f(x)=f(x+\alpha)$. In this case, the critical temperature $T_c(C)$ is determined from

$$4C^4K_1+12C^3(1-C)K_3+12C^2(1-C)^2K_5+4C(1-C)^3K_6=1$$

or

$$\tfrac{1}{8}C^4[\tanh(4t_0)+2\tanh(2t_0)]+\tfrac{3}{4}C^3(1-C)[\tanh(3t_0)+\tanh(t_0)]+\tfrac{3}{2}C^2(1-C)^2\tanh(2t_0)+C(1-C)^3\tanh(t_0)=\tfrac{1}{4}\ , \tag{18}$$

which is equivalent to the result derived by Matsudaira.[22] For clarification, in Fig. 6 the $T_c(C)$ is depicted as a function of concentration C. The critical concentration C^* is then given by $C^*=0.4284$, as noted in the preceding section.

By using Eq. (17), let us now investigate the reduced magnetization curves of the dilute ferromagnetic square lattice, in order to compare the magnetic behaviors of the diluted surface with those of the purely two-dimensional dilute ferromagnet. In Fig. 7, the temperature dependences of the reduced magnetization are shown for some values of concentration C. The effect of decreasing the concentration of magnetic atoms is an increase in the depression of magnetization over the entire temperature range for $T\le T_c$, which phenomenon is generally observed in diluted and amorphous ferromagnets. Very near the critical concentration C^*, however, the behavior of the reduced magnetization curve is rather different. The curve of $C=0.43$ is over that of $C=1$ (pure case) and shows an abrupt increase from the $T/T_c=1$ on decreasing the temperature. The result reminds us that of the reduced magnetization curve of a quasi-one-dimensional ferromagnet[23]; near the critical concentration the magnetic behavior of a diluted two-dimensional ferromagnet becomes like that of a one-dimensional system.

The above results in the diluted two-dimensional system have been discussed in some literatures. However, replotting the reduced magnetization as a function of concentration C for a fixed temperature, we found an interesting fact shown in Fig. 8. The reduced magnetization at absolute zero, as expected, takes a value of unity, independent of C until the critical concentration C^*. On the other hand, the reduced magnetization at a finite temperature at first decreases on decreasing the concentration and shows a minimum at a particular concentration. On passing the concentration, the curve then increases to a finite value at the critical concentration and at the point the reduced magnetization suddenly disappears, as expected in Fig. 7.

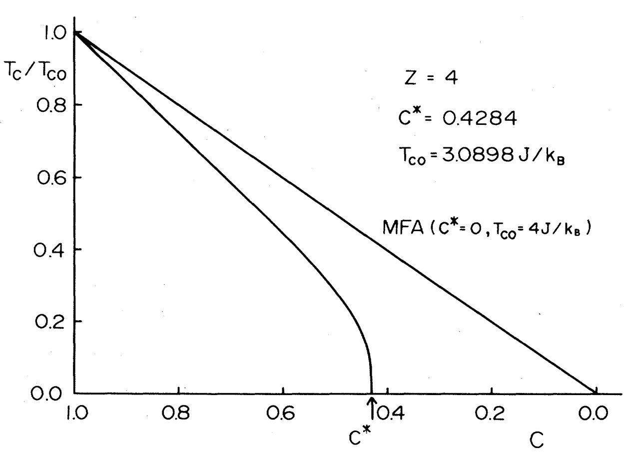

FIG. 6. Concentration dependence of the Curie temperature for the diluted square lattice. For comparison, the MFA result is also depicted.

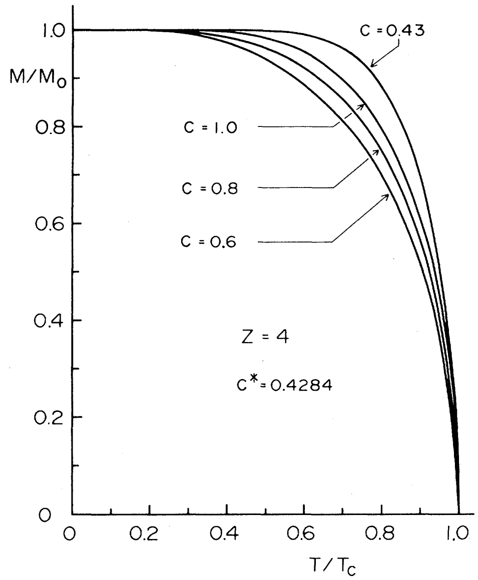

FIG. 7. Reduced magnetization curves vs the concentration C of magnetic atoms for the square lattice.

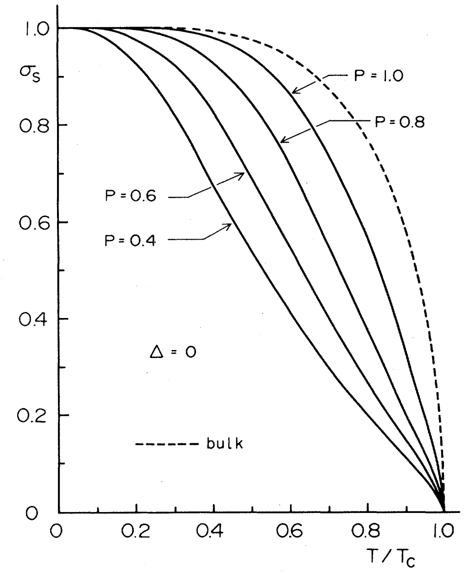

FIG. 9. Reduced magnetization curves of surface and bulk for $\Delta=0$, when the concentration P of magnetic atoms at the surface is change.

Approaching the critical temperature, the specific concentration showing a minimum in the curve gradually decreases to the critical concentration. To our knowledge the result is the first time. This may be found experimentally by replotting the available data of magnetization in dilute ferromagnets.

V. REDUCED MAGNETIZATION CURVES OF DILUTED SURFACE

In this section, let us again examine the magnetic behaviors of the Ising model with diluted (1,0,0) surface in a simple cubic lattice.

In the previous work for pure surface ($P=1$),[7] some of the present authors have discussed the temperature dependences of magnetizations σ_n given by Eqs. (6)–(8) by solving them numerically until eleven layers ($n=11$). Afterwards we also studied Eqs. (6)–(8) with $P=1$ numerically under the assumption that surface magnetization could be determined with enough precision even by terminating them at $n=3$.[8] From these works we found that even if we terminate them at $n=3$, the surface magnetization can be obtained with enough precision, while the bulk magnetization cannot precisely be estimated especially near the critical temperature. Therefore, for the evaluation of surface magnetization we here assume that from the third layer, the magnetization of each layer can be approximated by the bulk value, which is given by, on putting $\sigma_n=\sigma_{n+1}=\sigma_{n-1}=\sigma$ into Eq. (8),

$$\sigma=[\cosh(Dt)+\sigma\sinh(Dt)]^6\tanh x\,|_{x=0}\,. \tag{19}$$

The transition temperature T_c^b of the bulk can be evaluated from

$$1=6\sinh(Dt_c^b)\cosh^5(Dt_c^b)\tanh x\,|_{x=0}$$
$$=\tfrac{3}{16}[\tanh(6t_c^b)+4\tanh(4t_c^b)+5\tanh(2t_c^b)]\,, \tag{20}$$

with

$$t_c^b=\frac{J}{k_B T_c^b}\,,$$

which is nothing but the Zernike equation obtained for a ferromagnetic simple cubic Ising lattice.[16] The Curie temperature of (20) is given by $(k_B T_c^b)/J=5.076$, which is not close to the series value 4.5 for the simple cubic lattice, but to the value 4.933 for the Bethe method.[24]

Now, in order to evaluate the surface magnetization $\sigma_s\equiv\sigma_1$, it is necessary to solve the coupled equations (6), (7), and (19) numerically, under the assumption of $\sigma_3=\sigma$. The numerical results are shown in Figs. 9 and 10. As

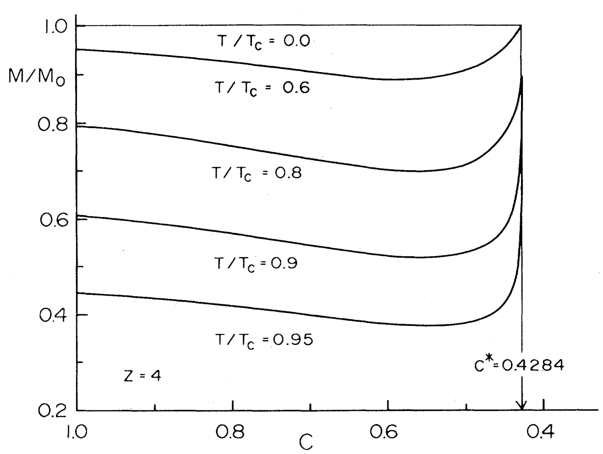

FIG. 8. Concentration dependence of the normalized magnetization for the diluted square lattice, in which the temperature is fixed at a given value. M_0 is the magnetization at absolute zero.

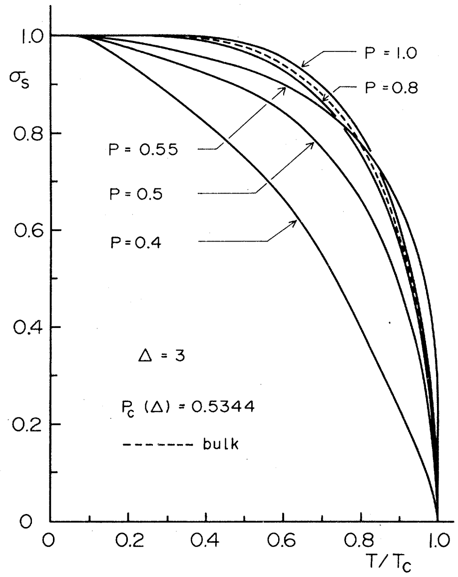

FIG. 10. Reduced magnetization curves of surface and bulk for $\Delta=3$. The critical value $P_c(\Delta)=0.5344$ is determined from the relation $\Delta_c(P)=3$, as shown in Fig. 3.

noted in Sec. III, for $\Delta > \Delta_c(P)$ the surface behaves like a bulk two-dimensional Ising system and for $\Delta < \Delta_c(P)$ the surface orders when the bulk does. Therefore, the reduced magnetization curves of surface are investigated for some fixed concentrations of surface magnetic atoms and especially for two cases, namely $\Delta=3$ and $\Delta=0$. In the figures, dashed lines express the reduced magnetization curve of bulk given by Eq. (19).

As understood from Figs. 3 and 5, for the case of $\Delta=0$ (or Fig. 9) the surface magnetic ordering is only possible when the bulk orders. Especially for $P=1$, the effect of surface is the depression of magnetization over the entire temperature range for $T \le T_c$, in comparison with that of bulk. Decreasing the concentration P of surface magnetic atoms, the magnetization shows a larger depression and almost the linear temperature dependence of surface magnetization is observed until rather low temperatures, in contrast with the behavior of the pure two-dimensional case (or Fig. 7). Experimentally, the linear temperature dependence of surface magnetization near a critical temperature has been found by means of low-energy electron diffraction (LEED), for instance, in antiferromagnetic NiO.[25] Thus, such a linear behavior of surface magnetization may be more preferably found on diluting the surface.

Here, especial attention should be paid for the case of $\Delta=3$ (Fig. 10), since, as shown in Fig. 3, surface magnetism is possible until the critical concentration $P_c(\Delta)=0.5344$ determined by the relation $\Delta_c(P)=\Delta=3$ and the surface may behave like a two-dimensional Ising model for $P > P_c(\Delta)$. In fact, the reduced magnetization curve for pure surface with $P=1$ in Fig. 10 and that for the two-dimensional ferromagnet with $P=1$ in Fig. 7 are equivalent to each other within their numerical errors, which implies that, as expected from Fig. 2, the pure surface with the restriction of $\Delta > \Delta_c$ behaves like a two-dimensional Ising model. However, the effect of surface concentration P on their reduced magnetization curves is rather different from that of two-dimensional systems.

Decreasing the concentration P of surface magnetic atoms, the reduced magnetization curve at first shows a weak depression of magnetization, in comparison with that of pure surface with $P=1$. Approaching the critical concentration $P_c(\Delta)=0.5344$, on the other hand, the curve of surface rapidly increases near the transition temperature, like that of the two-dimensional system, namely the curve of $C=0.43$ in Fig. 7. But at low temperatures the curve more swiftly decreases than that of bulk or pure surface, on increasing the temperature from absolute zero. Below the critical concentration $P_c(\Delta)=0.5344$, the surface magnetism is impossible in the Mills's sense. The surface only orders when the bulk does. Therefore, below the $P_c(\Delta)$ the behavior of the reduced surface magnetization curve is similar to that of Fig. 9. In contrast with Fig. 9, the reduced magnetization curve for $P=1$ in Fig. 10 is over that of bulk, since the surface orders before the bulk does and the surface behaves like a two-dimensional ferromagnet. Thus, for the case of $\Delta > \Delta_c$ we may find experimentally some interesting results of surface magnetization in the problem of surface dilution.

VI. CONCLUDING REMARKS

Our discussion has revealed some characteristic behaviors of magnetism in the Ising model with various concentrations of magnetic atoms at the surface. On dilution at the surface, the critical value $\Delta_c(P)$ showed an interesting behavior in the Mills's sense; the critical value P_c determined from the divergence of $\Delta_c(P)$ was not equal to the percolation concentration C^* of two-dimensional systems. Theoretically it is interesting to study what happens at the surface in the region of concentration between P_c and C^*. The concentration dependence of the transition temperature T_c^s for surface ordering was different from that of bulk. For the dilution at the surface the reduced magnetization curve of surface also exhibited some peculiar behaviors in comparison with that of bulk.

The theory of surface with randomly distributed magnetic atoms has not been studied in many papers, although there is a long history of research for the dilution of magnetic atoms in the bulk.[26] Most of the theoretical work on surface magnetism has been concerned with the temperature dependence of magnetization at the pure surface near the critical temperature, namely critical exponent β. Our theory is, however, based on the effective-field theory with correlation, so that it is impossible to discuss such a critical phenomenon at the diluted surface, which will be an another interesting problem.

Experimentally, our model may have some relevances with an amorphous magnetic layer deposited on a ferromagnetic crystalline system and ferromagnetic materials in which surface dilution can be produced artificially, e.g., by coating or ion implantation.

Finally, we hope that our study will stimulate further experimental and theoretical works on the system considered here. A comparison of our work with experiment should be worthwhile.

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APPENDIX

The coefficients A_ν ($\nu=1-9$), B_ν($\nu=1-2$), and C in Eqs. (9)—(11) are given as follows:

$$A_1=\cosh^3(Dt_s)\sinh(Dt_s)\cosh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_2=\cosh^4(Dt_s)\sinh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_3=\cosh^2(Dt_s)\sinh(Dt_s)\cosh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_4=\cosh^2(Dt_s)\sinh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_5=\cosh(Dt_s)\sinh(Dt_s)\cosh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_6=\cosh^2(Dt_s)\sinh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_7=\sinh(Dt_s)\cosh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_8=\cosh(Dt_s)\sinh(Dt)\tanh x\,|_{x=0}\,,$$

$$A_9=\sinh(Dt)\tanh x\,|_{x=0}\,,$$

$$B_1=\cosh^5(Dt)\sinh(Dt)\tanh x\,|_{x=0}\,,$$

$$B_2=\cosh^4(Dt)\sinh(Dt)\tanh x\,|_{x=0}\,,$$

and

$$C=B_1\,.$$

The coefficients can easily be calculated by applying a mathematical relation, $e^{\alpha D}f(x)=f(x+\alpha)$.

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$$\langle\sigma_i\rangle_r=\sum_{n=1}^{z}\binom{z}{n}P^n(1-P)^{z-n}\left\langle\tanh\left[\frac{J}{k_BT}\sum_{f=1}^{n}\sigma_f\right]\right\rangle\,,$$

especially for dilute ferromagnets with nearest-neighbor interaction J, as discussed in G. B. Taggert, Physica, 116A, 34 (1982). For bond dilution, see the discussions of the Appendix in T. Kaneyoshi and H. Beyer, J. Phys. Soc. Jpn. 49, (1980) 1306.

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