Monte Carlo simulations of the Curie temperature of ultrathin ferromagnetic films

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A Hamiltonian is considered that describes overlayers of classical Ising spins coupled to a polarizable substrate whose spins can take on continuous values. Monte Carlo simulation techniques are then used to study the temperature dependence of the magnetization for bcc lattices of mesh size 16×16 for a variety of coverages, coupling strengths, and overlayer morphologies. A primary motivation is to develop insights into the Fe thickness dependence of the Curie temperature measured experimentally for the Fe/Pd(100) system by Liu and Bader, especially the pronounced variation observed in the submonolayer Fe regime. We are able to capture the essential physics of the problem using a random-site-vacancy model, as opposed to a two-dimensional-island model, in accord with the results of recent photoemission efforts to characterize the morphology of the films.

Recent experimental advances have led to the observation of magnetic transitions in monolayer-range systems of magnetic materials adsorbed on metal surfaces.[1] These experiments allow the first generation of studies of two-dimensional (2D) phase transitions in epitaxial magnetic overlayers. Systems that have been studied include Fe/Au(100) (Ref. 2), Fe/Pd(100) (Ref. 3), V/Ag(100) (Ref. 4), Ni/Ag(100) (Ref. 5), and Gd/W(110) (Ref. 6). Because of the surface anisotropy in these systems, they are expected to show Ising-type critical behavior. And, indeed, 2D Ising exponents have been reported for many of these systems. For instance, the values (0.13–0.16) of the effective magnetization exponent extracted from experiments for Fe/Pd(100) are close to and consistent with the theoretical 2D Ising critical value of $\beta_c=\frac{1}{8}=0.125$. Nevertheless, the magnetic behavior of these thin films can be complicated by a number of factors related to interactions with their substrates. Depending upon the specific materials and coverages involved, these factors may include partial alloying at the interface, unknown distribution of the adsorbate atoms on the substrate, strain-layer epitaxy effects, and induced moments in normally nonferromagnetic substrates.[7]

In addition to the universal properties of the transition, the behavior of the Curie temperature T_C of ultrathin magnetic films has also been of long-standing as well as recent interest theoretically,[8,9] and experimentally.[3,5,10–13] In this work we are concerned with understanding qualitative features of the dependence of magnetic transition temperature on coverage for ultrathin films of Fe grown on Pd(100). The Fe-Pd(100) interface appears to experience minimal mixing.[14] However, the system is different than the other systems cited above in that the Fe induces a magnetic moment in the interfacial Pd atomic layers.[15] Using a simple spin model for this property we suggest a qualitative explanation for the experimentally observed behavior. In particular, we find that the measured dependence of T_C on Fe dosage can be understood most easily in terms of a random distribution of Fe atoms (or small clusters of atoms) on the Pd surface interacting with fluctuating Pd moments. This description of the morphology is in contrast to the common expectation that metallic adlayers, such as Fe, initially form 2D islands on metallic substrates such as Pd. Our results also provide an explanation of the results of recent photoemission efforts to characterize the morphology of the Fe/Pd system using a xenon physisorption approach,[16] as will be described.

In Fig. 1 the square symbols show the experimentally observed dependence of T_C on Fe dosage, as determined by surface magneto-optic Kerr-effect measurements.[3] The experimental results for T_C-vs-Fe dosage show a steep decrease below one monolayer (ML). Such a drop is *not* expected if the Fe exists as large, 2D islands on the Pd surface. In that case, T_C should display only modest finite-size broadening and shifting effects as the coverage is reduced.[17] Indeed, one would expect the transition at 0.4 ML to be little changed in temperature from that at 1.2 ML's, whereas experiment indicates that the transi-

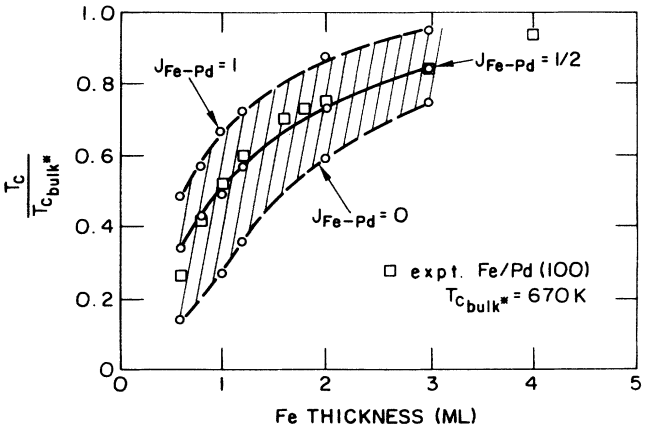

FIG. 1. Calculated T_C-vs-Fe dosage for the random-site-occupancy model with couplings $J_{\text{Fe-Pd}}=0$, 0.5, and 1.0 (for $J_{\text{Fe-Fe}}$ and $J_{\text{Pd-Pd}}$ held fixed at 1). The circles are the results of the actual Monte Carlo runs, and the curves and hatching are to guide the eye. The bulk T_C value is extrapolated from the experimental data (square symbols), and the asterisk denotes that the "bulk" corresponds to an epitaxially stabilized structure and not to α-Fe.

tion is suppressed below 100 K by the time that coverage is reached. For very low coverages ($\ll 1$ ML) T_C can be strongly altered due to additional considerations, such as reaching the percolation limit, and the increased relative importance of step- and kink-defect binding sites in determining the adlayer morphology. For the sake of simplicity, to minimize the influence of these considerations, we have concentrated our efforts on the high-coverage submonolayer regime.

Our proposed explanation for the T_C behavior shown in Fig. 1 has two main features: (i) The rapid drop in T_C for coverages under one monolayer is due to a random distribution of Fe atoms (or clusters) rather than to large 2D islands. (ii) The curvature of the T_C-vs-coverage dependence is due to the induced moments on the interfacial substrate sites, which enhances the T_C value for thin magnetic overlayers, but has no effect in the 3D limit. In order to illustrate these two effects, we have simulated a simple spin model consisting of a dilute Ising model on a substrate of polarizable spins. The simulations are not meant to provide a quantitative description of the Fe/Pd system and other models would certainly be possible. Indeed, this work provokes the question of the proper statistical mechanical model of the Pd spins and leaves this question open to experimental investigation.

We represent the Fe atoms as classical Ising spins. The Pd-induced moment is represented as a one-dimensional spin, which can take continuous values. The Hamiltonian contains three terms: a standard Ising Hamiltonian representing the Fe-Fe interaction, a term coupling the Ising and continuous spins representing the Fe-Pd interaction, and a term coupling the continuous spins to one another representing the Pd-Pd interaction. If the Fe-Pd coupling is turned off, the Pd system exhibits no magnetic ordering at any temperature, while the Fe system exhibits standard Ising behavior. The Hamiltonian is

$$\mathcal{H}=J_{\text{Fe-Fe}}\sum_{\text{NN}}(s_i-s_j)^2+J_{\text{Fe-Pd}}\sum_{\text{NN}}(s_i-\sigma_j)^2 +J_{\text{Pd-Pd}}\sum_{NN}(\sigma_i-\sigma_j)^2 , \quad (1)$$

where the s_i represent the Ising spins, the σ_i represent the continuous spins, the summations are over nearest neighbors (NN), and the Fe-Pd interaction couples only those spins at the interface. The Pd spins are placed in a square lattice. The Fe spins may occupy sites in the centers of these squares. The arrangement of atoms continues in a bcc arrangement. The Fe structure in the Fe/Pd(100) system is known experimentally to be body-centered tetragonal;[18] however, the neighbor distances are such that, to our level of approximation, it suffices to take all of the Fe-Fe interactions to be equal. We have deposited our Fe spins as follows: We choose a site at random and place a spin upon that site, if the site is in the *first* Fe layer. If the site is in an *upper* Fe layer, we check to see whether the four nearest-neighbor sites below it are occupied. If so, the spin is placed; if not, the spin is placed instead on the layer below.

We have studied this Hamiltonian using standard Monte Carlo simulation techniques on 16×16 lattices using a variety of coverages, coupling strengths, and deposition techniques. Most of the results reported are for unbounded Pd spins, i.e., $\mu=\infty$. Only relatively short runs of 500 attempts to flip each spin per temperature were required to obtain our results.

Our results for T_C vs dosage for such a system in which the Fe and Pd spins are uncoupled [$J_{\text{Fe-Pd}}=0$] are shown in Fig. 1. T_C is defined for this finite system as the point at which the magnetization falls below 0.5. Other definitions would be possible. However, the dependence of T_C on dosage is not significantly affected by the choice and we obtain good agreement in the submonolayer region with T_C values determined for a randomly dilute square lattice by other methods.[19,20] The behavior of the system for <1 ML is now qualitatively as observed experimentally. However, the increase of T_C with increasing thickness above 1 ML is too sharp in comparison to experiment.

We suggest that the flattening of the T_C-vs-dosage curve at higher Fe dosages in the simulation can be understood qualitatively by observing the results of turning on the Fe-Pd coupling. The most notable effect of this coupling is to raise the transition temperature (see Fig. 1). This effect can be understood quite simply if one notes that the partition function for the model may be exactly transformed, by integrating over the continuous spins, to an Ising system with longer-range interactions in the first layer. Thus, the effect of our idealized Pd is to provide coupling between more distant Ising spins; this increases the effective number of nearest neighbors and, thereby, increases the transition temperature.

Figure 2 shows the magnetization curve for a coverage of 1 ML with and without the Fe-Pd coupling. The T_C value is clearly much higher for the coupled system. However, as the Fe dosage is increased the effect of the Pd spins diminishes until the system reaches the appropriate bulk T_C value, as can be seen in Fig. 1. Figure 1 displays the results for T_C vs dosage for $J_{\text{Fe-Pd}}=0$, 0.5, and 1 (with $J_{\text{Fe-Fe}}$ and $J_{\text{Pd-Pd}}$ held fixed at 1). While no attempt has been made to match the experimental curve

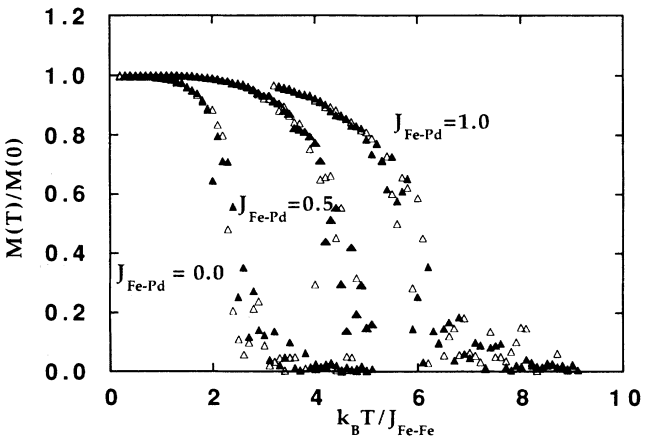

FIG. 2. Calculated magnetization curves for an Fe dosage of 1 ML with Fe-Pd coupling of 0, 0.5, and 1. Heating and cooling runs are denoted with open and closed symbols, respectively.

precisely, one can see that the effect of swiftly dropping T_C values at submonolayer dosages and the rather flat T_C values at higher dosages are nicely explained by our theoretical picture. It should be noted that the bulk T_C value in this case does not correspond to that of ordinary bcc α-Fe. This is, in part, because we are dealing with a strained system that is adjusted to the Pd lattice spacing.

Our random-site-occupancy model provides a description of the film morphology that differs from the common one involving 2D islands. It is of interest to note that there is additional experimental evidence that is consistent with our model. Recently, photoemission of physisorbed Xe on Fe/Pd(100) has been used as a novel probe of the film morphology.[16] This experiment monitors the way that a monolayer of Xe physisorbed onto the film references its emission spectrum with respect to that of the underlying substrate. The spectra of interest derive from the Xe $5p_{1/2,3/2}$ emission. If a 2D-island structure were present for submonolayer Fe coverages, the Xe 5p-spectrum would be expected to consist of two superimposed contributions, one from the Xe that is bound to Pd islands and one from Xe bound to Fe islands. Experimentally no spectral doubling was observed for any of the films studied, which included films grown at different temperatures, and for a variety of Fe dosages.[16] The Xe spectrum broadened and, in the thickest films, shifted by an amount consistent with expectations based on the work functions of the two metals but never doubled. This is interpreted as evidence that the films do not assume an island structure. For the random-site-occupancy model we do not expect the Xe spectrum to decompose into a few superimposed spectral components. Rather, a continuous spectral broadening is expected because the large Xe atom will average over mixed Fe-Pd sites, rather than distinct Fe or Pd regions. Thus, the Xe probe experiments are consistent with our model.

In our simulations presented above the σ_i are continuous and unbounded. The treatment of the Pd spins as continuous seems reasonable in light of electronic structure calculations,[15] which suggest a smooth variation of the zero-temperature Pd moment with distance from the Fe atoms. In these simulations the σ_i tend to take on the value of the neighboring Ising spins for $T < T_C$. Thus, the effect of thermal fluctuations on these artificial Pd spins is primarily to disorder rather than to dissolve them, and they do participate in the phase transition by enhancing the effective coupling between the Ising spins.

In an independent set of runs we have tested the sensitivity of the model to putting finite bounds on the σ_i. In the absence of coupling to the Ising overlayer, one would expect that the effect of finite bounds would be to bring about an entropic preference for a zero average moment chosen to permit the largest fluctuations. Thus, as the bounds are made more stringent, there will be a competition between the energetic preference for following the neighboring Ising spins and the entropic tendency for the moment to dissolve. In the simulations we found that when the σ_i are bounded close to $\mu=1$ they do dissolve from an induced moment of magnitude 1 at low temperatures to a low value near T_C. If the Pd moments dissolve

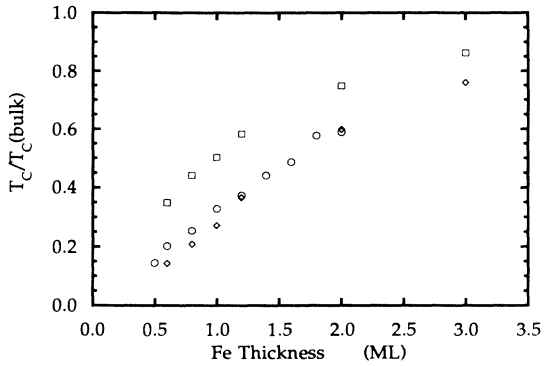

FIG. 3. Calculated T_C-vs-coverage plot for $J_{\text{Fe-Pd}}=0.5$, $\mu=\infty$ (square symbols), $J_{\text{Fe-Pd}}=0.5$, $\mu=1$ (circles), and $J_{\text{Fe-Pd}}=0$ (triangles). Note that when the Pd spins are strongly bounded that they effectively decouple from the Fe spins.

significantly at $T \ll T_C$, then they may be expected to have much less impact on the value of T_C.

This expectation is confirmed by our simulations in which the σ_i are bounded by $\mu=1$. The T_C-vs-coverage curve for this case is shown in Fig. 3 for $J_{\text{Fe-Pd}}=0.5$. Also, shown for comparison are the corresponding curves for unbounded Pd spins and for the case of no coupling between Fe and Pd. Note that for $\mu=1$ the Fe-Pd coupling has essentially no effect on the value of T_C. The qualitative agreement of our simulations for $\mu=\infty$ with the experimental results suggests that the Pd spins do retain a substantial moment near T_C. Finally, we note that for the model in which the Pd spin is restricted to discrete values, we would expect the T_C-vs-coverage behavior to be qualitatively similar to that of the $\mu=\infty$ case. This is because entropic suppression of the moment would be substantially lessened. Separate determination of the Fe and Pd magnetic behavior has not yet been experimentally feasible to resolve the question of whether significant induced Pd moments remain near T_C.

In summary, Monte Carlo calculations were performed for an Ising model that involves classic spins adsorbed on a substrate that takes on continuous spin values. The motivation was to provide insights into the T_C behavior of the system Fe grown on Pd(100), especially to understand the strong variations observed experimentally for submonolayer Fe coverages. Qualitative and even semiquantitative agreement was obtained with experiment for a random-site-occupancy model that was used to describe the morphology of the films. This same model is found to be consistent with the results of recent experimental efforts to characterize the morphology of the films, which were based on the photoemission spectra of Xe physisorbed on the Fe/Pd(100) films.

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[1]L. M. Falicov, D. T. Pierce, S. D. Bader, R. Gronsky, K. B. Hathaway, H. J. Hopster, D. N. Lambeth, S. S. P. Parkin, G. Prinz, M. Salamon, I. K. Schuller, and R. H. Victora, J. Mater. Res. **5**, 1299 (1990).

[2]W. Dürr, M. Taborelli, O. Paul, R. Germar, W. Gudat, D. Pescia, and M. Landolt, Phys. Rev. Lett. **62**, 206 (1989); W. Dürr, D. Kerkmann, and D. Pescia, Int. J. Mod. Phys. B **4**, 401 (1990).

[3]C. Liu and S. D. Bader, J. Appl. Phys. **67**, 5758 (1990).

[4]C. Rau, G. Xing, and M. Robert, J. Vac. Sci. Technol. A **6**, 579 (1988); C. Rau, Appl. Phys. A **49**, 579 (1989).

[5]C. A. Ballentine, R. L. Fink, J. Araya-Pochet, and J. L. Erskine, Appl. Phys. A **49**, 459 (1989).

[6]M. Farle and K. Baberschke, Phys. Rev. Lett. **58**, 511 (1987).

[7]C. Liu and S. D. Bader, J. Vac. Sci. Technol. A **8**, 2727 (1990).

[8]K. Binder and P. C. Hohenberg, IEEE Trans. Magn. **MAG-12**, 66 (1976).

[9]M. Bander and D. L. Mills, Phys. Rev. B **38**, 12 015 (1988).

[10]M. Stampanoni, Appl. Phys. A **49**, 449 (1989).

[11]C. M. Schneider, P. Bressler, P. Schuster, J. Kirschner, J. J. de Miguel, and R. Miranda, Phys. Rev. Lett. **64**, 1059 (1990).

[12]D. P. Pappas, K. P. Kämper, and H. Hopster, Rev. Lett. **65**, 2058 (1990).

[13]W. Weber, D. Kerkmann, D. Pescia, D. A. Wesner, and G. Güntherodt, Rev. Lett. **64**, 1059 (1990).

[14]C. Liu and S. D. Bader, J. Magn. Magn. Mater. **93**, 307 (1991).

[15]S. Blügel, M. Weinert, and P. H. Dederichs, Phys. Rev. Lett. **60**, 1077 (1988); S. Blügel, B. Drittler, R. Zeller, and P. H. Dederichs, Appl. Phys. A **49**, 547 (1989).

[16]S. D. Bader and C. Liu, J. Vac. Sci. Technol. A **9**, 1924 (1991).

[17]D. P. Landau, Phys. Rev. B **13**, 2997 (1976).

[18]J. Quinn, Y. S. Li, D. Tian, F. Jona, and P. M. Marcus, Phys. Rev. B **43**, 3959 (1991).

[19]W. Y. Ching and D. L. Huber, Phys. Rev. B **13**, 2962 (1976).

[20]R. B. McQuistan, J. Li, and J. L. Hock (private communication).