Thin films of itinerant-electron ferromagnets on a nonmagnetic metallic substrate

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(Received 5 March 1979)

We report a simple theory of a film, no more than a few atoms thick, of an itinerant ferromagnet deposited on a semi-infinite nonmagnetic metallic substrate. The magnetic properties of such a film are described by the use of Hubbard's model Hamiltonian for a narrow *s* band and the substrate is represented as an uncorrelated *s*-band metal. The screened, single-site interaction term in Hubbard's Hamiltonian is decoupled in the Hartree-Fock approximation. Consequent to this description, the magnetic moments in those layers of the film immediately adjacent to the interface are found to be strongly dependent on the value chosen for the nearest-neighbor transfer-matrix element connecting the film and the substrate. For the case when the film is a monatomic layer, its moment is found to disappear altogether if that transfer-matrix element is sufficiently, yet not unreasonably, large. Furthermore, the moment is found to vanish much more readily for films which have a nearly filled band (as in nickel) than for those with an approximately half-filled band (as in iron). In thicker films, the lowest one or two layers have essentially similar properties. Overall, this theory leads to results which agree reasonably well with the recent observations of Bergmann upon films of nickel, cobalt, or iron on the nonmetallic substrate Pb_3Bi.

I. INTRODUCTION

Recently, Bergmann[1] has made a series of very careful measurements of the anomalous Hall effect at low temperatures in ultrathin films of iron, cobalt, or nickel condensed on the nonmagnetic amorphous metal substrate Pb_3Bi. From these measurements, he has been able to infer the net magnetization of the films, and its dependence upon their thickness. In the case of nickel, he discovered that, when the film was less than a critical depth, approximately two and a half atomic layers (the thickness being averaged over the film can be given in fractional units), it supported no measurable magnetic moment. However, as the film approached this critical thickness, its susceptibility increased as if to diverge. Indeed, further increase in the thickness of this film produced spontaneous magnetization (see Fig. 1). In dramatic contrast to nickel, a "coverage of only $\frac{1}{6}$th atomic layer of iron yielded a nonlinear temperature-dependent Hall curve," indicative of a nonzero magnetic moment. The results for cobalt were similar to those for iron. Measurements of the dependence of the superconducting transition temperature of the substrate-film composite upon the film's thickness also corroborated such a picture for the film magnetization.

One of us[2] has recently used a variant of Hubbard's Hamiltonian[3] for a correlated, narrow *s* band to determine conditions for the pinning of a

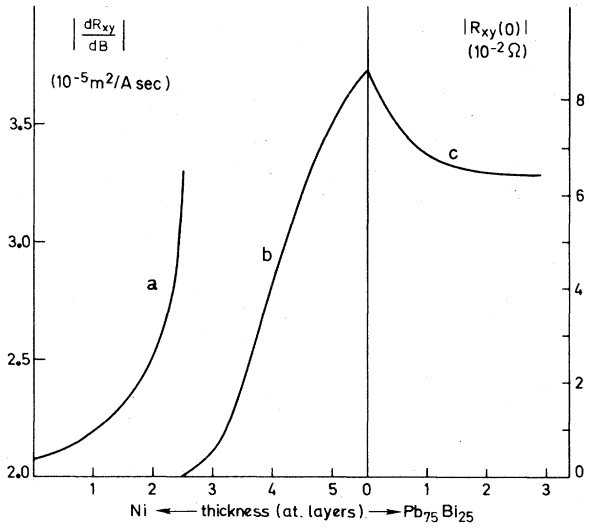

FIG. 1. These curves are taken directly from Bergmann (Ref. 1), although his data points are not reproduced explicitly: *a*, the initial slope with increasing field of the (linear) Hall effect (which is proportional to the susceptibility) as a function of thickness of the nickel films. *b*, the anomalous Hall resistance extrapolated to zero field (which is proportional to the magnetic moment) of the Pb_3Bi-Ni combination. *c*, as *b* when further layers of Pb_3Bi are superposed on a nickel film 5.6 atomic layers thick.

domain wall at a planar defect—an antiphase boundary—in itinerant ferromagnets such as Cu_2MnAl and MnAl. (See, for example, Lapworth and Jakubovics[4]; also Ziljstra and Haanstra.[5]) The pinning can be explained substantially in terms of the phase diagram obtained by Penn[6] for the relative stabilities of the ferromagnetic, antiferromagnetic, and paramagnetic solutions to the Hartree-Fock description of Hubbard's Hamiltonian. There, it is shown that, for systems with an approximately, but not exactly, half-filled band, ferromagnetic ordering is stable at high values of the ratio U/W (Coulomb correlation energy to bandwidth), and that as U/W decreases there is a first-order transition to an antiferromagnetic state. Thus, a planar defect in an otherwise ferromagnetic material can, by introducing a two-dimensional bound state, enlarge the effective bandwidth in its immediate vicinity, thereby lowering the effective ratio U/W, and self-consistently making stable a brief span of the antiferromagnetic state; in other words, a domain wall is thus spontaneously created. Such a simple description of these systems is also supported by the fact that, *a priori* calculations of the ratio U/W for the transition metals[7] when used with Penn's phase diagram, give a satisfactory description of the known magnetic properties of these *d*-band transition metals.

In this paper analogous simple arguments will be put forward to explain the results deduced from the beautiful experiments of Bergmann.[1] Disappearance of the magnetization in the first one or two layers of a nickel film will be thus understood in terms of a local increase in the effective bandwidth, which would arise from the assumption that the nearest-neighbor transfer-matrix element across the interface of film and substrate is larger than those prevailing within the film itself. The disparity observed between the films of iron and cobalt on the one hand, and nickel on the other, will be explained in terms of the known larger band occupancy of nickel.

II. THE MODEL

The model is defined on a simple cubic lattice in the tight-binding approximation. The system is translationally invariant over the x-y plane and repeats with a unit cell containing a large number of sites in the z direction. Of these n sites, the parameters for the extreme two are chosen so that they mimic free space. As a consequence, successive cells are decoupled from one another. The next m sites at either end are chosen to correspond to the m atomic layers of the magnetic film, and the remaining, intervening sites represent the semi-infinite substrate. Thus the interface of interest occurs twice in each cell, a consequence of the periodic method of solution adopted here, which greatly facilitates the computational aspects of the problem. So long as the total number of atoms in the cell, n, is large and the thickness of the magnetic film, m, is small, the periodicity can be expected to be irrelevant. That this is indeed so will be demonstrated retrospectively in Sec. III.

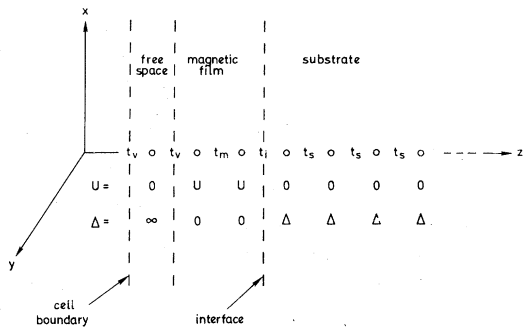

FIG. 2. One end of the unit cell of the model for the case of a magnetic film of two atomic layers.

After inverse lattice transformations, the double-time, retarded Green's function[8] of the three-dimensional system described above is characterized through the matrix equation

$$(\omega \underline{I} - U\underline{\bar{n}}_{-\sigma} - \underline{T})\underline{G}^{\sigma\vec{k}} = \underline{I} \ . \tag{2.1}$$

Here ω is the electron energy and $\vec{k}$ its momentum; $\bar{n}_{l-\sigma}$ is the average occupation of a Wannier state of spin σ. Note, $\sigma = \uparrow$ or $\downarrow$ on the lth site; Hubbard's interaction energy U is nonzero at magnetic sites (layers) and zero elsewhere; and the transfer matrix $\underline{T}$ has nearest-neighbor (off-diagonal) elements of value t_m coupling successive magnetic layers (if there be more than one), a generally different value, t_s, coupling the nonmagnetic layers of the substrate, another value t_i across the interface, and a vanishing value t_v (in practice $<10^{-3}$ of t_m or t_s) between the ultimate (free space) and penultimate sites of each cell. (See Fig. 2.) The ultimate sites are guaranteed zero occupation by the addition there of a large spin-independent potential (a work function) to the appropriate diagonal element of $\underline{T}$. The diagonal elements of $\underline{T}$ include also the terms $2t_l(\cos k_x + \cos k_y)$, which, for a simple cubic lattice, entail the only appearance of the components k_x and k_y of momentum, manifesting motion parallel to the interface. If the intralayer matrix element t_l is assumed to be independent of the layer position, l, and is equal to t, say, then one achieves the great simplification that the energy ω can be partitioned into contributions ω_z, arising from motion perpendicular to the interface and $\omega_{xy} = 2t(\cos k_x + \cos k_y)$, arising from motion parallel to it. Note that the bands created by $\underline{T}$ in the film at the interface and the substrate can still be given arbitrarily different widths through the choice of the parameters for interlayer hoppings, t_m, t_i, and t_s. The only other nonzero elements of $\underline{T}$ are

$t_v e^{\pm ink_z}$, and describe the vanishingly small end-to-end interaction between successive cells.

With the energy partitioned, Eq. (2.1) becomes the one-dimensional problem for determining the Green's function, $G_{ll'}^{\sigma k_z}$, as a function of the partial energy ω_z. The corresponding one-dimensional site densities of states can then be calculated and the three-dimensional site densities of states $\rho_l(\omega)$ found by folding it in with the x-y density of states—the latter being that of the tight-binding approximation of a square lattice. The $\rho_l(\omega)$ are then integrated up to the Fermi energy, and the procedure is iterated until the resultant expectation occupations, $\bar{n}_{l\sigma}$, for all layers l within the cell are determined self-consistently.

The characteristic differences between the parameters of the magnetic film and those of the substrate would, in general, lead to a flow of charge across the interface. This "junction" effect would, in turn, establish a dipole potential which would act to preserve overall charge neutrality on a macroscopic scale. In the present model, this effect is imitated by adding a constant, spin-independent potential, Δ, to each site in the substrate, so that the junction dipole potential is a step function. The parameter Δ then is determined self-consistently by the requirement that the total occupation of, say, the substrate site furthest from the defect exactly equals the prescribed value in a perfect crystal. It is then found that even on a local scale, only small deviations from charge neutrality occur. Moreover it is found that Δ is virtually independent of the interface transfer-matrix element t_i and the number n of atoms in the cell (note that n is large compared to 1) and only weakly dependent on the number m of (potentially magnetic) atomic layers in the film (m is, of course, of the order of unity).

III. REMARKS ON THE MODEL

The transition metals iron, cobalt, and nickel all have d-band widths of about 6 eV, whereas the conduction band in Pb_3Bi arises from s and p orbitals, and ought therefore to be much wider. Therefore, most of the present calculations were carried out with the magnetic interlayer transfer integral t_m equal to one quarter the corresponding interlayer transfer integral in the substrate, t_s, and the uniform intralayer transfer integral, t, set equal to t_m. This choice gives the bandwidth in the substrate to be twice that in the film, which is a reasonable choice for the system in hand. The correlation energy U was taken initially to be $12t$, i.e., the bandwidth in the transition-metal layers. The occupancy of 1.18 electrons/atom was chosen for the substrate, that is to say a band just over half-filled, which we expect would be a qualitatively reasonable parametrization of the Pb_3Bi substrate.

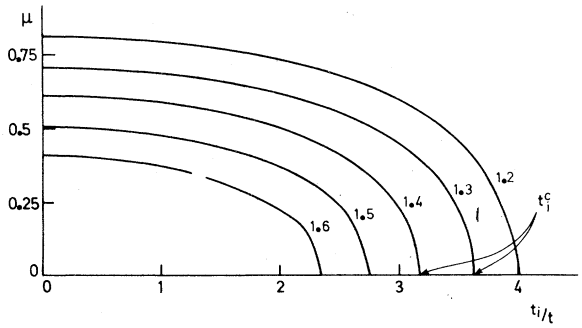

FIG. 3. Magnetic moment per atom of a monolayer film as a function of t_i, for various occupancies of the band in the film as marked. The bandwidth of the substrate is taken as twice that of the magnetic material, and the band occupancy of the substrate as 1.18 electrons/atom.

With other parameters so set, the dependence of the magnetic moment in a monolayer film upon the occupancy of the magnetic band and the interface transfer-matrix element t_i is found to be as shown in Fig. 3. While the curves for different magnetic-band occupancies all show the anticipated second-order transition, as t_i increases, into the paramagnetic state, the critical abscissa t_i^c at which the moment disappears is strongly dependent on the occupancy. Thus a monolayer of nickel, which one might associate with the case 1.6 electrons/atom in Fig. 3, would lose its moment when the hybridizing perturbation of the interface is comparatively moderate, whereas a similar perturbation would cause only a small change in the moment of a monolayer of cobalt (1.4 electrons/atom) and even less in one of iron (1.2 electrons/atom). On the other hand, the value of U appropriate for iron or cobalt is undoubtedly less than that for nickel,[7] which ought to imply a reduction in t_i^c for each of those elements from that indicated by Fig. 3. However, it transpires that the calculated variation of t_i^c with reasonable changes in U is far less than its variation with band occupancy, which reflects the steep slope of the ferromagnetic-paramagnetic phase boundary in the parameter space of U/W and band occupancy for the perfect crystal.[6] When U is reduced to $9t$, which is appropriate for iron relative to the value $12t$ taken for nickel, t_i^c for a band occupancy of 1.2 electrons/atom turns out to be $\sim 3t$, which is still considerably greater than t_i^c for nickel in Fig. 3. Therefore the predicted distinction between nickel and iron or nickel and cobalt remains.

Next, these calculations were repeated for the case when the substrate's interlayer matrix element t_s is set equal to t_m (and t), so that the bandwidths in film and substrate are equal. For this case, we again obtained a set of curves qualitatively similar to those in Fig. 3.

The dependence of the model's characteristics

upon the choice of substrate parameters was further tested with calculations for a substrate band occupancy of 0.5 electrons/atom. It was found that, although the curves were somewhat flatter than those in Fig. 3, approaching the t_i axis more obliquely, the values of t_i^c were changed by no more than 10%. Thus, one expects at least a qualitative invariance in the observed behavior of films under changes of substrate as long as the substrate is metallic with a bandwidth similar to or a few times larger than that of the magnetic film and a band occupancy of the order of 0.5 to 1.5 electrons/atom.

Returning to the case when the substrate bandwidth is twice that of the film and its occupancy is approximately that of Pb_3Bi, moments in each layer of a film of two atomic layers were calculated again as functions of t_i and magnetic band occupancy. In Fig. 4, the magnetic moments in the ferromagnetic solution for a two-layer film with these parameters are plotted. The layer adjoining the substrate can be seen to have a moment in Fig. 3, but develops a tail after it reaches a small value. It is as though it remains supported by the moment in the next layer, which, even for the highest magnetic-band occupancies shown, does not quite vanish even for the highest reasonable values of t_i. This is to be compared with Bergmann's observation that 2.5 layers of nickel possess no moment. However, in view of the fact that the nearest-neighbor tight-binding picture undoubtedly underestimates the range of the interactions being modeled, which must be crucial in determining the depth of film which the perturbing presence of the interface can penetrate, this quantitative discord should not be considered as being too severe a drawback. We have therefore tested a model with second-nearest-neighbor interactions which leads, as anticipated, to the absence of a moment in a double atomic layer of nickel.

It might also be added that other magnetic solutions are possible in the present model. One such reasonable solution would have antiparallel moments but nonzero net magnetization which is, in fact, a possibility not completely excluded by Bergmann's observations. For such a solution, we have found universally that the moments in both layers vanish more rapidly with increasing t_i than those shown in Fig. 4 for the purely ferromagnetic solution being described here.

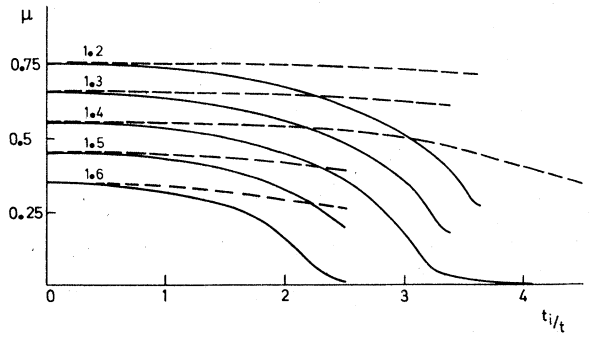

FIG. 4. Magnetic moments per atom of the layer next to the interface (full curve) and the second layer (dashed curve) of a two layer film as a function of t_i for various band occupancies as marked. The substrate properties were taken as in Fig. 3.

For films of three and more layers, in the completely ferromagnetic solution the two layers nearest to the substrate have moments virtually identical to those for the two-layer film. The subsequent layers possess a moment nearly independent of t_i. However, in a model with longer-range interactions, one would expect the addition of further magnetic layers on top of a two-layer film to have some effect on the moments in those two lowest layers.

A. "Sandwich" problem

Bergmann conducted a further experiment in which he covered a film of nickel 5.6 atomic layers thick with a second deposit of Pb_3Bi. As the thickness of this superstrate increased, the magnetization of the sandwiched nickel film was seen to decrease (Fig. 1), but apparently not to zero. To describe this situation, a calculation was made of the effect upon a magnetic film three layers thick of adding a single, further layer of the model Pb_3Bi. It was found generally that the moments of both the uppermost and bottom layers of the magnetic film were reduced, much as the moment is reduced in the nearest layer by a single interface; while the moment of the middle magnetic layer was only slighly less than it would have been in the absence of the superstrate. However, the solution of this calculation depends strongly upon the dipole potential assumed to exist across the new interface. This dependence arises from the concomitant flow of charge across that interface, which alters directly the occupation of the magnetic film, and thus the moments therein (cf., Figs. 3 and 4). As the superstrate increases in thickness from a monolayer, its bandwidth increases, approaching that of the substrate, and at the same time the dipole moment across the new interface must approach that across the film-substrate interface. Unfortunately, there is no simple means of deciding precisely what the new dipole moment should be, because there is no reason to insist upon charge neutrality in a monolayer superstrate. Therefore, a quantitative matching of the right-hand half of Fig. 1 remains beyond the small scope of this model. However, it is clear that two mechanisms could contribute to the observed reduction of the magnetization as the superstrate is thickened: namely, the (uncertain) charge flow described above, and the direct dilation of the bands in the

magnetic layers caused by their coupling to the widening bands of the superstrate.

All of the above calculations were performed over a unit cell (Fig. 2) of either 24, 36, or 48 sites. The calculated moments were independent of the size of the cell to within 2%. However, it was sometimes necessary to use the largest cell, which yields smoother functions for the site densities of states, to avoid numerical instabilities when tracking the ferromagnetic solution over the entire range of t_i.

IV. CONCLUSIONS

We have presented a reasonably plausible model of a magnetic film interfaced with a semi-infinite metallic substrate, which is at once simple and contains the essential features of the physics of the problem. We have found that the principal dependence of the magnetic moments lies jointly with the degree of band hybridization occurring at the interface (measured by t_i) and with the electronic population of the magnetic film itself.[9] Moreover, variation with changing Coulomb correlation energy U is less rapid than the variation with band occupancy. For a plausible choice of the parameter t_i, the model describes adequately the fact that moment is lost in thin layers of nickel and not of cobalt or iron. This description is qualitatively unaffected by quite a wide variation of the parameters chosen to describe the metallic substrate.

The site density of states for the magnetic layer adjoining the interface increases in width rapidly with increasing t_i, irrespective of whether or not the substrate band has been chosen to be wider than that in the film. This suggests that, in the tight-binding approximation, one may speak sensibly of a bandwidth pertaining to a single layer, defined essentially by the immediately surrounding transfer-matrix elements. Then, in a model Hamiltonian such as Hubbard's, which attributes magnetic ordering to the density of states at the Fermi level and the relative size of the intra-atomic correlation U to the bandwidth W, a distinct ratio U/W can prevail in each layer. Then Figs. 3 and 4 manifest simply the reduction of magnetic moment as W increases and U/W is lowered towards the critical value which, for given band occupancy, divides the ferromagnetic and paramagnetic states.

A weak point of the model is its naive treatment of the dipole potential formed across the interface and the associated transfer of charge, which affects directly the predicted critical value t_i^f at which the moment of a monolayer disappears. However, although the present characterization of the junction effects of iron, cobalt, or nickel upon Pb_3Bi are *ad hoc* and oversimplified, the errors so introduced can reasonably be expected to be similar for the three metals, which have roughly analogous electronic structures. The representation of differences in the behavior of films of these systems is therefore qualitatively correct.

ACKNOWLEDGMENT

Financial support from the U. K. Science Research Council and the National Science Foundation under Grant No. DMR 77-11257 is gratefully acknowledged.

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[9]Absence of a moment in the Ni layers might be attributed to the dimensionality in that it is known that ideal two-dimensional systems with isotropic interactions do not sustain long-range order at finite T (Ref. 10). However, in this system some anisotropy is expected and interactions via the semi-infinite substrate are important. Moreover, this argument would not explain the variation of the layer properties with thickness and the moment seen in monatomic layers of Fe and Co.

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