Surface magnetism in an exactly soluble many-body periodic-cluster model of bcc iron

Changfeng Chen

Department of Physics, University of Oregon, Eugene, Oregon 97403*;
and Department of Physics, University of California, Berkeley, California 94720;
Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

An exact solution of a two-dimensionally periodic two-site cluster, a {001} two-layer thin film with body-centered-cubic (bcc) crystal structure, is presented for iron. The purpose is to study the surface magnetism of bcc iron in a full many-body approach. The model consists of five d orbitals per site per spin, with interatomic hopping terms, a one-electron occupation energy for each orbital, and an on-site Coulomb interaction of the fullest generality allowed by atomic symmetry. A realistic local-density-approximation single-particle electronic structure is used. Crystal-field effects in the iron-film structure are discussed. The many-body energy-level spectrum and thermodynamic averages of energy and spin of the system are calculated. The physical picture for the enhancement of magnetization at the true iron surface is discussed.

I. INTRODUCTION

The study of magnetism at the surface of transition metals has been a very active field in recent years because of both the fundamental and the technological importance of these materials. Intense research activities have been carried out for various metals, alloys, and chemisorbed systems.[1] Earlier experiments[2] showed that Fe, which is a bulk ferromagnet of magnetic moment $2.22\mu_B$ (μ_B is the Bohr magneton) per atom,[3] had a magnetically "dead" (i.e., paramagnetic) surface. This result stimulated great interest in understanding mechanisms which determine the surface magnetism of transition metals. Later transmission Mössbauer spectrum measurements[4] at ultrathin Fe(110) film indicated that the appearance of surfaces actually enhances the magnetization at surface layers of Fe. The observation of the magnetically dead surface is now believed[5] to be due to contaminated Fe surfaces.

A theoretical understanding of the enhancement of magnetization at Fe surfaces presents the challenge of a full many-body problem. Transition metals have a very narrow one-electron d-band width, which is of magnitude comparable with the intra-atomic Coulomb interaction. As a consequence, both band-structure effects and the Coulomb interaction must be properly taken into account in any calculation. However, this is practically intractable, because of the large number of particles in a macroscopic crystal. The traditional way of dealing with this problem takes the one-particle picture as basic and includes many-body effects only in the form of a suitably averaged single-particle exchange-correlation potential. This approach has been successful in explaining properties of both bulk crystals[6-11] and clusters.[12,13] A fairly good result of the enhancement of magnetization at the Fe(001) surface has also been achieved[14] by using this approach. However, there are also exceptions, which involve many-body effects that cannot be taken into ac-

count by this sort of averaging. A well-known example is the valence-band photoemission satellite,[15] approximately 6 eV below the Fermi level, in face-centered-cubic Ni. A successful theoretical treatment,[6] among others,[17] to this problem was introduced by Victora and Falicov in a periodic small-cluster approach.

The purpose of this paper is to carry out a full many-body calculation to investigate the surface magnetism of Fe, and find the "driving force" for the enhancement of magnetization at Fe surfaces. It would be interesting to know what the roles of the two competitive effects, i.e. band-structure effects and many-body interactions, are in determining the electronic and magnetic properties of this highly correlated system in the presence of surfaces. The method used in this work is the periodic small-cluster approach.[16] It treats the band-structure effects and the electron-electron interaction on an equal footing. It has been successfully applied to various systems where local many-body effects are important: the photoemission behavior in bulk[16] and surface[18] Ni; magnetic properties of bulk Fe, Co, and the Fe-Co alloy;[19,20] intermediate-valence behavior in Ce;[21,22] alloying in the Cu-Ag-Au system;[23] electronic, magnetic, and superconducting properties of a heavy-fermion system;[24-26] a four-atom cluster Hubbard model;[27] and the electron-lattice interaction in the Hubbard model;[28] as well as thermodynamic properties[29,30] and valence-bond formation.[31] In this approach, a model Hamiltonian which explicitly includes band-structure effects and many-body interactions is solved exactly. The problem is made tractable by modeling the sample as a finite-size crystal with periodic boundary conditions. This is equivalent to solving exactly a many-body problem with integrals in k space restricted to a limited sampling. It has proved to be very good at determing spatially uniform and short-range properties. Because of the limited size of the cluster, one would not expect to get a sharp phase transition in this approach, but indications of possible mechanisms

involved in long-range correlations can also be obtained. The computational overhead is drastically reduced by the full use of group-theoretical techniques.

The rest of this paper is arranged as follows. Section II presents the Hamiltonian and discusses the crystal-field effects in the Fe-film structure. Section III describes the method of calculation. Section IV presents and discusses the results. The conclusions are summarized in Sec. V.

II. THE HAMILTONIAN

The Hamiltonian for bulk Fe metal is described in Ref. 19. Here the same two-atom cluster, the smallest non-trivial bcc crystal, is chosen, but with periodic boundary conditions applied only in a two-dimensional plane to form a two-layer Fe film with (001) orientation (see Fig. 1). The z axis is perpendicular to the film. This is equivalent to a restricted sampling of one point in the surface Brillouin zone (SBZ), i.e. the γ point, the center of SBZ. In this structure, each atom has only four nearest neighbors instead of eight as in the bulk bcc crystal, i.e. only the four in the adjacent layer survive. There are five d orbitals per atom per spin; in the presence of a cubic field, as in bulk Fe metal, these orbitals split into a triplet t_{2g} and a doublet e_g. In the two-layer bcc structure discussed here the environment for each atom is radically different from that in a bulk bcc crystal. The d orbitals further split into more energy levels. This crystal-field effect is one of the major features of the results obtained here.

The model Hamiltonian contains both single-particle and two-particle terms:

$$H = \sum_{\substack{i,j;\mu,\nu;\sigma \\ (i\neq j)}} t_{i\mu,j\nu} c_{i\mu\sigma}^{\dagger} c_{j\nu\sigma} + \sum_{i,\mu,\sigma} E_{\mu} c_{i\mu\sigma}^{\dagger} c_{i\mu\sigma}$$

$$+ \sum_{i;\mu,\nu,\lambda,\phi;\sigma,\sigma'} V_{\mu\nu\lambda\phi} c_{i\mu\sigma}^{\dagger} c_{i\nu\sigma'}^{\dagger} c_{i\lambda\sigma'} c_{i\phi\sigma} . \qquad (2.1)$$

Here i,j ($=1,2$) label atoms in the cluster; μ,ν,λ,ϕ ($=1,2,3,4,5$) label the five d orbitals; and σ,σ' are spin labels. The single-particle hopping terms $t_{i\mu,j\nu}$ are parametrized according to the Slater-Koster scheme.[32] Note that the two-atom cluster allows for only nearest-neighbor hopping; in the restricted crystal the second-
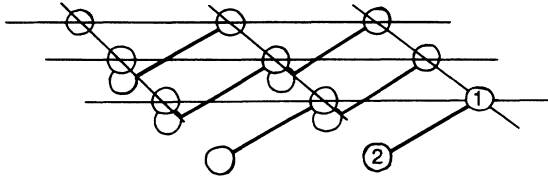

FIG. 1. The two-atom cluster in the two-layer bcc structure. With periodic boundary conditions this cluster, which forms an infinite two-layer slab, is equivalent to sampling the surface Brillouin zone at the zone center γ (see the text for details). For each site in the cluster, there are only four nearest neighbors, instead of eight as in the bulk bcc structure.

nearest neighbor of an atom is identical to itself. The intra-atomic Coulomb interactions $V_{\mu\nu\lambda\phi}$ most generally allowed by atomic symmetry[33] are used. They include a direct Coulomb integral U, an average integral

$$J = \tfrac{1}{2}[J(e_g,e_g) + J(t_{2g},t_{2g})] ,$$

and an exchange anisotropy

$$\Delta J = J(e_g,e_g) - J(t_{2g},t_{2g}) .$$

Following Ref. 19, a value of U is chosen to be 4.9 eV and the other interaction parameters are set in the ratios $U:J:\Delta J = 56:8:1$. (The results are insensitive to the exact values of these ratios.) The next largest contribution is the nearest-neighbor Coulomb term, which in the cluster makes a constant contribution and can be neglected.

It is clear that the crystal-field effect is, in the dilayer, quite different from that of the bulk, because the atoms in these "surface" layers have fewer neighbors. A straightforward calculation shows that, in the case of bulk Fe metal, the energy shift of the doublet e_g and the triplet t_{2g} caused by crystal-field effects can be expressed as

$$\Delta E_{e_g} = -\tfrac{32}{15} d_{1NN} + \tfrac{12}{5} d_{2NN} , \qquad (2.2a)$$

$$\Delta E_{t_{2g}} = \tfrac{64}{45} d_{1NN} - \tfrac{8}{5} d_{2NN} , \qquad (2.2b)$$

where

$$2 \Delta E_{e_g} + 3 \Delta E_{t_{2g}} = 0 , \qquad (2.3)$$

and d_{1NN} and d_{2NN} are the contributions to the energy shift from each of the first and second neighbors, which must be determined before the crystal-field splitting in the two-layer Fe-film structure can be calculated. From the Eqs. (2.2) and the value of the d-level splitting in the bulk Fe one obtains an equation relating d_{1NN} and d_{2NN}. To determine d_{1NN} and d_{2NN}, one more condition is necessary. It is assumed that

$$d_{2NN}/d_{1NN} = (dd\sigma)_2/(dd\sigma)_1 . \qquad (2.4)$$

Although this assumption is not rigorous, it is physically quite reasonable. The values of $(dd\sigma)_2$ and $(dd\sigma)_1$ are taken from the fit data given in Ref. 19. It gives $(dd\sigma)_2/(dd\sigma)_1 = 0.594$. Thereby one can easily get, from the bulk data analysis, $d_{1NN} = -0.246$ eV and $d_{2NN} = -0.146$ eV. (In this contribution, energies are measured in eV below the Fermi level of bulk Fe metal, unless otherwise indicated.)

By applying the same crystal-field-effect analysis, the energy shifts in the case of the two-layer Fe-film stucture are obtained,

$$\Delta E_{\alpha} = -\tfrac{16}{15} d_{1NN} + \tfrac{4}{15} d_{2NN} , \qquad (2.5a)$$

$$\Delta E_{\beta} = -\tfrac{16}{15} d_{1NN} + \tfrac{44}{15} d_{2NN} , \qquad (2.5b)$$

$$\Delta E_{\gamma} = \Delta E_{\delta} = \Delta E_{\varepsilon} = \tfrac{32}{45} d_{1NN} - \tfrac{16}{15} d_{2NN} , \qquad (2.5c)$$

where the subscripts α, β, γ δ, and ε refer to the five d orbitals of symmetries $(r^2 - 3z^2)$, $(x^2 - y^2)$, xy, yz, and zx, respectively. The position of the d levels of the Fe-film

TABLE I. Hamiltonian parameters (energies are in eV *below* the Fermi level of bulk Fe metal). The subscripts $\alpha, \beta, \gamma, \delta$, and ε refer to the d orbitals of symmetries $(r^2 - 3z^2)$, $(x^2 - y^2)$, xy, yz, and zx, respectively.

$(dd\sigma)$	0.771
$(dd\pi)$	−0.508
$(dd\delta)$	0.091
E_α	1.211
E_β	0.822
E_γ	0.969
E_δ	0.969
E_ε	0.969
U	4.9
J	0.7
ΔJ	0.088

structure can be easily obtained. All the parameters in the Hamiltonian (2.1) for the film are summarized in Table I. It should be emphasized here that the crystal-field calculations are made so as to keep constant the center of gravity of the d manifold. The large change found for the $(x^2 - y^2)$ orbital is in fact caused by a consistent change by the other four orbitals and a large resulting motion of the center of gravity.

Since metallic Fe has a magnetic moment of $2.22\mu_B$ per atom (Ref. 3) and the method allows only an integral number of particles in the cluster, the configuration chosen is four d holes in the neutral state of the cluster. In this configuration, there is an average of two holes per atom; therefore the maximum possible magnetic moment per atom is $2.00\mu_B$. The s-like conduction band of Fe metal can be treated as an electron reservoir which has "absorbed" four electrons and is not explicitly included in the calculation.

III. METHOD OF CALCULATION

With five d orbitals per atom per spin, there are 20 orbitals in the two-atom cluster. Simple combinatorial arguments yield 4845 states for four holes in the cluster. Clearly, the two-atom cluster model for Fe has a very large manifold of states. The symmetries inherent in the

Hamiltonian (2.1) must be exploited to reduce the size of the matrices to be diagonalized. In fact, there are many symmetries in the system. First, total spin in the cluster is a good quantum number. For the case of four holes in the cluster, there are 825 singlets, 990 triplets, and 210 quintets. Furthermore, there is also a space-group decomposition, which is very efficient in reducing the matrix size.

The space group for the two-layer, two-atom cluster (Fig. 1) is a nonsymmorphic one, or order 8. The origin of the coordinates is chosen at site 1. There is only one translation (the indentity translation) in the cluster. There are two fourfold and one twofold rotations around the z axis $(C_{4z}, C_{4z}^2, C_{4z}^{-1})$. There are also four twofold screw axes parallel to the x-y plane (their rotation part is formed by one of the four point operations $C_{2x}, C_{2y}, C_{2d}, C_{2d'}$). This nonsymmorphic space group possesses five irreducible representations with the following degeneracies: γ_1 $(d = 1)$, γ_2 $(d = 1)$, γ_3 $(d = 1)$, γ_4 $(d = 1)$, γ_5 $(d = 2)$. These representations correspond to the center of the two-dimensional square Brillouin zone (which extends over the region $-2\pi/a < \pm k_x \pm k_y \leq 2\pi/a$, where a is the cubic lattice constant of the bcc structure). The character table of the group[34] is given in Table II.

The two-layer structure discussed here can be obtained directly from the original bulk structure discussed in Ref. 19 by symmetry reduction. There are compatibility relations between the irreducible representations of the group of the two-atom cluster bcc bulk structure and those of the two-layer structure (see Table III). With a complete set of matrices that transform according to these irreducible representations,[35] it is possible to project out sets of symmetrized basis states. Since the representations cannot mix, this is equivalent to a block diagonalization of the Hamiltonian. In the case of four holes in the cluster, the largest block is 252×252, a considerable reduction from the original 4845×4845 matrix. The various block sizes are shown in Table IV. The solutions obtained by diagonalizing these blocks are exact solutions of the full Hamiltonian for the cluster.

IV. RESULTS AND DISCUSSIONS

In the earlier Fe work,[19] two different sets of Slater-Koster parameters are used. The first set is chosen to

TABLE II. The character table of the two-atom-cluster nonsymmorphic space group for the two-layer thin-film structure of Fig. 1. The symbol τ stands for the vector which connects the two atoms in the cluster. Note that τ is *not* a translational operation in the system.

	1 E	1 C_{4z}^2	2 C_{4z}, C_{4z}^{-1}	2 C_{2x}, C_{2y} τ	2 $C_{2d}, C_{2d'}$ τ
γ_1	1	1	1	1	1
γ_2	1	1	−1	1	−1
γ_3	1	1	1	−1	−1
γ_4	1	1	−1	−1	1
γ_5	2	−2	0	0	0

TABLE III. Compatibility relations between the representations of the group for the bulk structure and those for the group of the two-layer thin-film structure. The original representations are given in Ref. 19.

Original representations of the bulk structure	Reduce to the following representations of the two-layer structure
Γ_1	γ_1
Γ_2	γ_2
Γ_3	$\gamma_1 \oplus \gamma_2$
Γ_4	$\gamma_3 \oplus \gamma_5$
Γ_5	$\gamma_4 \oplus \gamma_5$
H_1	γ_3
H_2	γ_4
H_3	$\gamma_3 \oplus \gamma_4$
H_4	$\gamma_1 \oplus \gamma_5$
H_5	$\gamma_2 \oplus \gamma_5$

TABLE V. One-particle eigenvalues (energies are in eV *below* the Fermi level of bulk Fe metal) for two-layer bcc Fe-film structure. The degeneracies shown in the table are per spin.

Energy	Symmetry	Degeneracy
−0.410	γ_2	1
−0.021	γ_1	1
0.229	γ_2, γ_5	3
1.709	γ_4, γ_5	3
2.054	γ_4	1
2.443	γ_3	1

reproduce, in the absence of interactions, the calculated paramagnetic local-density-approximation band structure of Moruzzi et al.[36] at Γ and H points. This set of parameters models an *unsaturated* ferromagnet. The second set of parameters is different from the first set by an *artificial* shift of the e_g and t_{2g} levels to get a fully saturated ferromagnet. It is shown in this work that a fully saturated ferromagnet can be produced by the presence of surfaces.

A useful way to understand the many-body calculation is taking a Hubbard-model-like interpretation in which the single-particle energy levels are shifted by the exchange interaction J into single-particle majority- and minority-spin levels.[37] This is, of course, only an approximate picuture, since in the full many-body approach configuration interaction mixes all one-particle levels; nevertheless, this does provide a clear physical picture.

From the analyses in Ref. 19, it is known that the reason for obtaining an *unsaturated* bulk ferromagnet by fitting the band-structure result is that the exchange splitting is not sufficient to bring the highest one-electron (h_5, which can accommodate three electrons or holes of each spin orientation) majority-spin level below the closest minority-spin level. Therefore the fourth hole ends up in the majority-spin h_5 level, and thus produces an unsaturated ferromagnet. The one-particle levels of the two-layer Fe-film structure are presented in Table V. One can see that in the two-layer Fe-film case the d-band is shrunk and the one-particle energy levels split and rearrange themselves as the result of the appearance of surfaces. The top three levels are separated by 0.64 eV,

which is smaller than the exchange splitting $J = 0.70$ eV. When Coulomb interaction is turned on, the spin states split by approximately J, which is now sufficient to bring all the majority-spin levels of the top three one-particle energy levels below the lowest minority-spin level of γ_2/γ_5 symmetries. (The other three one-particle energy levels are too far away to matter). Therefore, in the ground state the four holes in the cluster are all in minority-spin levels, i.e., one in γ_2, one in γ_1, and two in the γ_2/γ_5 manifold. It is thus expected that the ground state of the Fe film is a fully saturated ferromagnet. This is consistent with the calculated many-body ground state of $^5\gamma_4$ symmetry.

It is clear from the above analyses that while Coulomb interaction is an essential requirement for the formation of ferromagnetic ground states, the *change* from the unsaturated bulk ferromagnet to the saturated surface (thin-film) ferromagnet (i.e., the enhancement of magnetization at surfaces) in Fe is dominated by one-particle parameters (band-structure effects), i.e., the band narrowing and the crystal-field effects. This may give a better understanding of the fact that the band-structure calculation[12] works fairly well on the surface magnetization problem of this highly correlated system.

The many-body density of states (MBDOS) is the best way to show the spectrum of energy eigenvalues of the Hamiltonian (2.1). At each eigenvalue,[38] a peak of weight equal to the degeneracy at that energy is plotted. In a finite system, this results in a discrete set of spikes, which have been broadened artificially into a Gaussian of 0.1 eV half-width. Figure 2 shows the MBDOS of the two-layer Fe film. Comparing with the bulk result[19] one can immediately see that the spectrum is shifted toward the Fermi level and most weights of MBDOS are close to the Fermi level. This shift is a direct consequence of the band narrowing and the one-particle level rearrangement due to the appearance of surfaces.

The periodic small-cluster model can also provide the

TABLE IV. Sizes of blocks of the various representations for the two-layer thin-film-structure space group.

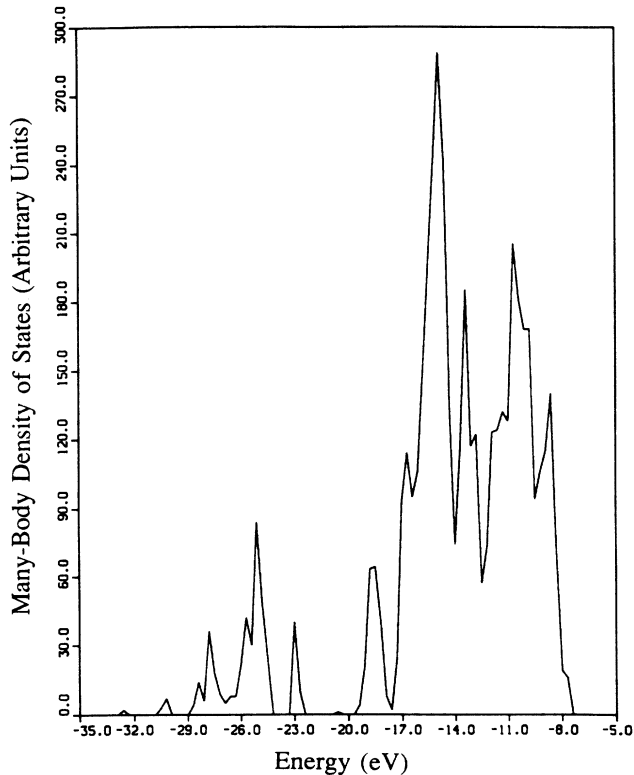|	γ_1	γ_2	γ_3	γ_4	γ_5
$S = 2$	31	27	21	27	52
$S = 1$	117	121	127	121	252
$S = 0$	119	106	94	106	200

FIG. 2. The eigenvalue spectrum (many-body density of states) for the two-layer Fe film. In this plot, energies are measured in eV *above* the Fermi level of bulk Fe metal, E_F^{bulk}. The negative values here correspond to energies *below* E_F^{bulk}.
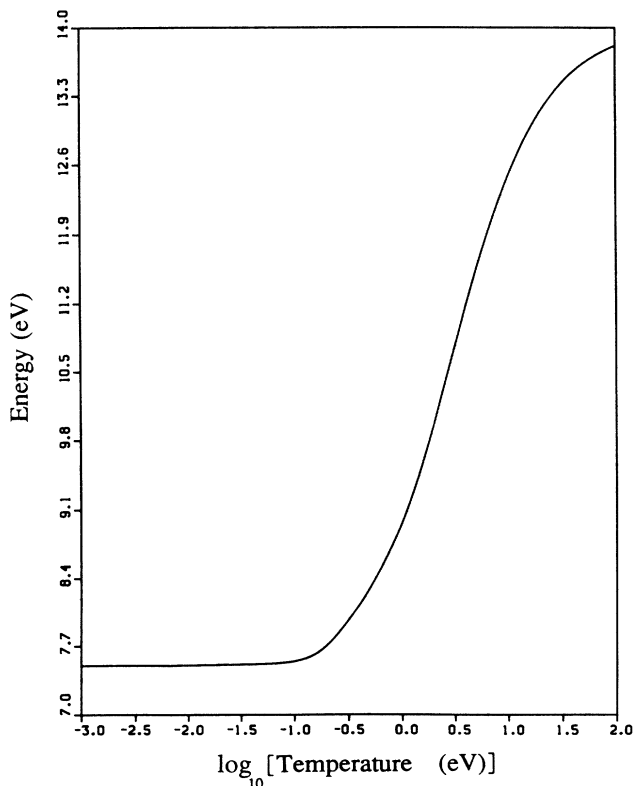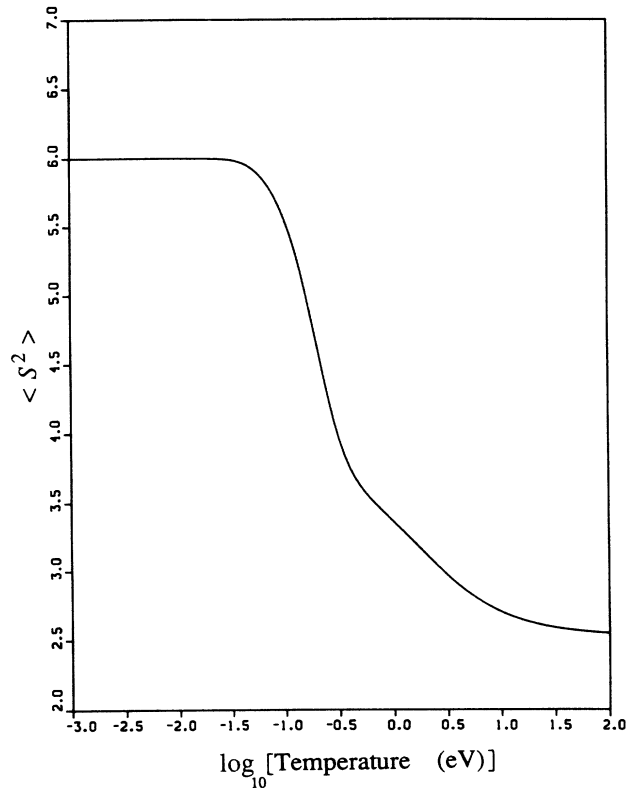

FIG. 4. The thermodynamic average of S^2 for the two-layer Fe film.

eigenstates, allowing one to compute various thermodynamic quantities as functions of temperature. This is done by simply calculating the desired quantities for each eigenvalue, multiplying by the appropriate Boltzmann factor, and adding.

In this work, thermodynamic averages of energy E and spin square S^2 of the Fe film are calculated. Results are presented in Figs. 3 and 4. These results are similar to those of the saturated ferromagnet given in Ref. 19, where an *artificial* shift of e_g and t_{2g} levels is applied. However, there are also some differences between the two sets of results. First of all, the energy value is much smaller in the present Fe-film calculation, due to the band narrowing and the crystal-field effects discussed above. Secondly, as temperature decreases the $\langle S^2 \rangle$ curve in the present contribution raises much steeper than the result given in Ref. 19 for the saturated ferromagnet. The appearance of these differences is actually quite natural: the electronic structure of the present Fe film is of course very different from that of the bulk[19] with just a shift of one-particle occupation energies, although both systems have fully saturated ferromagnetic ground states.

V. CONCLUSION

A many-body periodic-cluster model of $3d$ electrons for a {001} dilayer of bcc Fe has been studied to explore the modification of electronic structures and the enhancement of magnetization in the presence of surfaces. This approach incorporates both band-structure effects and

FIG. 3. The thermodynamic average of energy for the two-layer Fe film.

many-body interactions on an equal footing. This model is undoubtedly too simple to reproduce all the rich electronic and magnetic behavior of this important metal; however, it presents an exactly soluble model for such a highly correlated system, and gives accurate information about some properties; it especially provides a clear physical picture to understand the mechanism which determines the surface magnetism of this system.

It is found that crystal-field effects play an important role in determining the essential features of the electronic structure in the presence of surfaces. The ground-state properties are dominated by the one-particle terms in the Hamiltonian. The enhancement of magnetization at Fe surfaces is shown to be due to the change of one-particle energy levels at surfaces, although Coulomb interaction is an essential requirement for the formation of ferromagnetic ground states. On the other hand, there is no doubt that the electron-electron interactions are important in determining some other properties, e.g. photoemission behavior and band narrowing as observed for other systems.[16-19]

Improvements to the model have been considered. It is believed[20] that three d holes per Fe atom is more sensible for the "weak" ferromagnet Fe. In this case there are six d holes in the two-atom cluster. The ground state is an unsaturated bulk ferromagnet of magnetic moment $2.00\mu_B$ per atom, which is very close to the experimental value of $2.22\mu_B$ per atom.[3] Also there is still room for

flipping the majority-spin hole to produce a fully saturated ferromagnet at surfaces. This scheme will of course give a much better description of the surface properties of Fe. However, preliminary calculations showed that one has to expand the size of the cluster to get the extra room for flipping the majority-spin hole. Unfortunately, the number of many-body states (i.e., the size of the Hamiltonian) increases exponentially with the size of the cluster. A four-atom cluster, the next smallest one for bcc structure, has approximately 10^{10} states for six holes in the cluster, which is impossible to handle by use of any currently available computer, even after the factorization by the full use of group-theoretical techniques. The present model is restricted to very small clusters; nevertheless, it is very helpful to predict general trends and get a clear physical picuture for highly correlated systems.

ACKNOWLEDGMENTS

*Present address.

[1]See, for example, *Magnetic Properties of Low-Dimensional Systems*, edited by L. M. Falicov and J. L. Moran-Lopez (Springer-Verlag, Berlin, 1986).

[2]L. N. Liebermann, D. R. Fredkin, and H. B. Shore, Phys. Rev. Lett. **22**, 5391 (1969); L. N. Liebermann, J. Clinton, P. M. Edwards, and J. Mathon, *ibid.* **25**, 232 (1970).

[3]C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 465.

[4]J. Tyson, A. H. Owens, and J. C. Walker, J. Appl. Phys. **52**, 2487 (1981).

[5]H. Hasegawa, in Proceedings of the Second International Workshop on Magnetic Properties of Low-Dimensional Systems (to be published).

[6]R. A. Tawil and J. Callaway, Phys. Rev. B **7**, 4242 (1973).

[7]C. S. Wang and J. Callaway, Phys. Rev. B **15**, 298 (1977).

[8]J. Callaway and C. S. Wang, Phys. Rev. B **16**, 2095 (1977).

[9]C. S. Wang, R. E. Prange, and V. Korenman, Phys. Rev. B **25**, 5766 (1982).

[10]H. S. Greenside and M. A. Schlüter, Phys. Rev. B **27**, 5 (1983).

[11]K. B. Hathaway, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **31**, 12 (1985).

[12]K. Lee, J. Callaway, and S. Dhar, Phys. Rev. B **30**, 1724 (1984).

[13]E. M. Haines, V. Heine, and A. Ziegler, J. Phys. F **15**, 661 (1985); **16**, 1343 (1986).

[14]S. Ohnishi, A. J. Freeman, and M. Weinert, Phys. Rev. B **28**, 6741 (1983).

[15]S. Hufner and G. K. Wertheim, Phys. Lett. **51A**, 299 (1975); C. Guillot, Y. Ballu, J. Paigne, J. Lecante, K. P. Jain, P. Thirty, R. Pinchaux, Y. Petroff, and L. M. Falicov, Phys. Rev. Lett. **39**, 1632 (1977); D. E. Eastman, F. J. Himpsel, and J. A.

Knapp, *ibid.* **40**, 1514 (1978); F. J. Himpsel, J. A. Knapp, and D. E. Eastman, Phys. Rev. B **19**, 2919 (1979); L. A. Feldkamp and L. C. Davis, Phys. Rev. Lett. **43**, 151 (1979); W. Eberhardt and E. W. Plummer, Phys. Rev. B **21**, 3245 (1980); L. A. Feldkamp and L. C. Davis, *ibid.* **22**, 3644 (1980); R. Clauberg, W. Gudat, E. Kisker, E. Kuhlmann, and G. N. Rothberg, Phys. Rev. Lett. **47**, 1314 (1981); L. C. Davis, J. Appl. Phys. **59**, 25 (1986).

[16]R. H. Victora and L. M. Falicov, Phys. Rev. Lett. **55**, 1140 (1985); for a general review of the periodic small-cluster method, see L. M. Falicov, in *Recent Progress in Many-Body Theories*, edited by E. Pajanne and R. Bishop (Plenum, New York, 1988), Vol. I, p. 275.

[17]D. R. Penn, Phys. Rev. Lett. **42**, 921 (1979); A. Liebsch, *ibid.* **43**, 1431 (1979); N. Martensson and B. Johansson, *ibid.* **45**, 482 (1980); L. C. Davis and L. A. Feldkamp, Solid State Commun. **34**, 141 (1980); A. Liebsch, Phys. Rev. B **23**, 5203 (1981); L. Kleinman and K. Mednick *ibid.* **24**, 6880 (1981); G. Treglia, F. Ducastelle, and D. Spanjaard, J. Phys. (Paris) **43**, 34 (1982); T. Aisaka, T. Kato, and E. Haga, Phys. Rev. B **28**, 1113 (1983); R. Clauberg *ibid.* **28**, 2561 (1983).

[18]C. F. Chen and L. M. Falicov, Phys. Rev. B **40**, 3560 (1989).

[19]E. C. Sowa and L. M. Falicov, Phys. Rev. B **35**, 3765 (1987).

[20]E. C. Sowa and L. M. Falicov, Phys. Rev. B **37**, 8707 (1988).

[21]A. Reich and L. M. Falicov, Phys. Rev. B **34**, 6752 (1986).

[22]J. C. Parlebas, R. H. Victora, and L. M. Falicov, J. Phys. (Paris) **47**, 1029 (1986).

[23]A. Reich and L. M. Falicov, Phys. Rev. B **36**, 3117 (1987).

[24]A. Reich and L. M. Falicov, Phys. Rev. B **37**, 5560 (1988).

[25]A. Reich and L. M. Falicov, Phys. Rev. B **38**, 11 199 (1988).

[26]C. F. Chen, A. Reich, and L. M. Falicov, Phys. Rev. B **38**, 12 823 (1988).

[27]L. M. Falicov and R. H. Victora, Phys. Rev. B **30**, 1695 (1984).

[28]C. R. Proetto and L. M. Falicov, Phys. Rev. B **38**, 1754 (1988).

[29]J. Callaway, D. P. Chen, and R. Tang, Z. Phys. D **3**, 91 (1986); Phys. Rev. B **35**, 3705 (1987).

[30]J. Callaway, D. P. Chen, D. G. Kanhere, and P. K. Misra, Phys. Rev. B **38**, 2583 (1988).

[31]J. Callaway, Phys. Rev. B **35**, 8723 (1987).

[32]J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954); corrected and extended to include higher angular momentum by R. R. Sharma, Phys. Rev. B **19**, 2813 (1979).

[33]M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964).

[34]L. P. Bouckaert, R. Smoluchowsky, and E. Wigner, Phys. Rev. **50**, 58 (1936).

[35]A. W. Luehrmann, Adv. Phys. **17**, 1 (1968).

[36]V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[37]Any use of the words "majority" and "minority" in the context of the spin orientation of an energy level refers to *electronic* spin, not the spin of the hole. In particular, if the spin orientations of all the holes in the ground state are the same, these holes are in minority-spin levels.

[38]The MBDOS should not be confused with the usual single-particle DOS; here the eigenvalues are the energies of many-body states rather than single-particl excitation energies.