

Surface photoemission and inverse photoemission in a periodic-cluster model of bcc iron: A many-body solution

Changfeng Chen

Department of Physics, University of Oregon, Eugene, Oregon 97403

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Results of an exact many-body calculation of photoemission and inverse-photoemission spectra are reported for a two-layer bcc Fe(001) thin film in a two-site crystal model with periodic boundary conditions. The object is to study the many-body electronic structure of Fe in the presence of surfaces. Realistic local-density-approximation one-electron structures of Fe are used. Intrasite electron-electron interactions most generally allowed by atomic symmetries are introduced. It is shown that crystal-field effects and the associated changes in the single-particle electronic structure play an important role in determining the many-body electronic structure in the presence of surfaces. Many-body correlation effects in the surface case are found to be stronger than those in the bulk. The relevance of the calculated results to experiment is discussed.

I. INTRODUCTION

The surface-electronic structure of transition metals has been a subject of great interest for a long time for both theoretical and technological reasons. Experimentally, photoemission (PE) and inverse-photoemission (IPE) measurements provide very detailed information about electronic structures in solids,¹ both in the bulk and at the surface. These measurements are especially useful in probing the details of electronic structure in solids with strong electronic correlations. Significant progress in understanding the mechanisms determining the properties of transition metals has not been made until recent years. Major theoretical difficulties are caused by the strong correlations between the d electrons. In many transition metals the ratio of the Coulomb repulsion energy between the d electrons to the d -band width is close to unity; it might be even larger at surfaces due to band narrowing. At this ratio, many-body effects have to be carefully treated in any electronic-structure calculation. The conventional way of doing this is to take the single-particle picture as a basis and include many-body effects only in the form of a suitably averaged single-particle exchange-correlation potential. This approach has been very useful in explaining many properties of bulk,²⁻⁶ surfaces,⁷ and clusters.^{8,9} However, there are exceptions which typically involve many-body effects. In valence-band PE (IPE) experiments on many transition metals (e.g., Ni, Co, Fe, etc.), there are "satellite" peaks observed in the energy range below (above) the bottom (top) of the valence band predicted by band-theoretical calculations involving local-density approximations. The most well-known example is the valence-band PE satellite¹⁰ approximately 6 eV below the Fermi level in fcc Ni. Much theoretical attention¹¹ has been focused on this feature, as well as other many-body corrections to the Ni density of emitted states; one successful treatment by Victoria and Falicov¹² uses a periodic-small-cluster method.¹³ Later, this method was applied to study PE,

IPE, and fluctuations in bulk Fe (Ref. 14) and revealed some important features of many-body effects therein. Most recently, it was used to study the surface magnetism of bcc Fe (Ref. 15) and the surface and thin-film PE spectra of Ni metal.¹⁶ The results give a clear physical picture of the enhancement of magnetism at Fe surfaces and predict the surface PE behavior of Ni metal.

The periodic-small-cluster method is a full many-body approach. It treats the band-structure effects and electron-electron interactions on an equal footing. In addition to the examples mentioned above, it has also been successfully applied to various problems¹⁷⁻²⁵ where local many-body effects are important. 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 solid as a limited-size crystal with periodic boundary conditions. This is equivalent to solving a many-body problem with integrals in \mathbf{k} space restricted to a limited sampling. It has proved to be very good at determining spatially uniform and short-range properties. Because of the limited size of the cluster, one would not expect to get a sharp phase transition and a good description for any property with nonuniform long-range characteristics 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.

In this paper the periodic-small-cluster method is applied to study the PE and IPE behavior of a two-layer Fe-film system. The purpose is to modify the approach of Ref. 14 so as to study the surface-electronic structure of Fe. Iron is an interesting case because it has more holes per atom than Ni, as well as a different crystal structure; it is also a prototypical ferromagnet. Although it has been pointed out²⁰ that a modified model is more suitable for Fe than that discussed in Ref. 14, one can see from the reported results^{14,20} that the average energy, average spin expectation value, and charge and spin fluctuations

in the cluster are very similar in these two models. Furthermore, it has been shown¹⁵ that the latter model¹⁴ provides a reasonably good starting point to get a correct picture for the surface-magnetization enhancement at Fe surfaces. Thus it is believed that the model introduced in Ref. 14 and used (after modifications for the surface structure) in this paper is at least an acceptable approximate one to study the properties of Fe surfaces. The reason for using this model instead of that in Ref. 20 is that, if more holes per atom are introduced as in Ref. 20, one has to deal with, in the surface case, a very large Hamiltonian matrix which cannot be handled on any existing computer system, even after factorization by the use of group-theoretical techniques.

The rest of this paper is organized as follows. In Sec. II we describe the model Hamiltonian and the method of diagonalizing it; in Sec. III we present the calculated results of PE and IPE spectra. A clear physical picture of many-body effects in the Fe-surface (thin-film) system is drawn. The relevance of the results to experiment is discussed. Conclusions are given in Sec. IV.

II. THE MODEL HAMILTONIAN

The model Hamiltonian for bulk bcc Fe is discussed in Ref. 14. Here the same two-atom cluster, the smallest nontrivial bcc crystal, is chosen, but with periodic boundary conditions applied only in a two-dimensional plane to form an infinite 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 the SBZ. In this structure each atom has only four nearest neighbors instead of eight as in a bulk bcc crystal. There are five d orbitals per atom per spin; in the presence of a cubic field, as in a bulk bcc crystal, these orbitals split into a triplet t_{2g} and a doublet e_g . In the two-layer bcc structure discussed here the local environment for each atom is radically different from that in a bulk bcc crystal. As a result, the energies of all five d orbitals are shifted and split into more (three) energy levels. This crystal-field effect is one of the major features of the results obtained here.

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

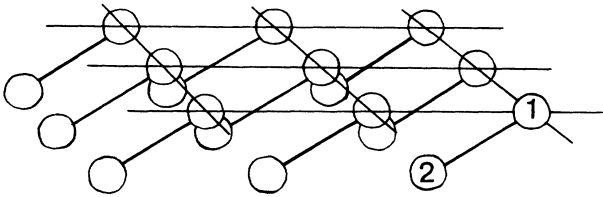


FIG. 1. Two-atom cluster in the two-layer bcc structure. With periodic boundary conditions applied in the two-dimensional plane, this cluster, which forms an infinite two-layer slab, is equivalent to sampling the surface Brillouin zone at the zone center γ (see the text for details).

$$H = \sum_{\substack{i,j;\mu,\nu;\sigma \\ (i \neq j)}} t_{i\mu,j\nu} c_{i\mu\sigma}^\dagger c_{j\nu\sigma} + \sum_{i;\mu;\sigma} E_{\mu} c_{i\mu\sigma}^\dagger c_{i\mu\sigma} + \sum_{i;\mu,\nu,\lambda,\phi;\sigma,\sigma'} V_{\mu\nu\lambda\phi} c_{i\mu\sigma}^\dagger c_{i\nu\sigma'}^\dagger c_{i\lambda\sigma} c_{i\phi\sigma}. \quad (2.1)$$

Here i, j ($=1, 2$) label atoms in the cluster; μ, ν, λ, ϕ ($=1, 2, 3, 4, 5$) label the five d orbitals; σ, σ' are spin labels. The single-particle hopping terms $t_{i\mu,j\nu}$ are parametrized according to the Slater-Koster scheme.²⁶ Note that the two-atom cluster allows for only nearest-neighbor hopping; in the restricted crystal the second-nearest neighbor of an atom is identical to itself. The intra-atomic Coulomb interactions $V_{\mu\nu\lambda\phi}$ most generally allowed by atomic symmetry²⁷ are used. They include a direct Coulomb integral U , an average exchange integral

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

and an exchange anisotropy

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

Following Ref. 14, the value of U is chosen to be 4.9 eV and the other interaction parameters are set in the ratio $U:J:\Delta J = 56:8:1$. (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 the energy shifts of the five d orbitals caused by the crystal-field effects in the thin-film case can be written as

$$\Delta E_\alpha = -\frac{16}{15}d_{1n} + \frac{4}{15}d_{2n}, \quad (2.2a)$$

$$\Delta E_\beta = -\frac{16}{15}d_{1n} + \frac{44}{15}d_{2n}, \quad (2.2b)$$

$$\Delta E_\gamma = \Delta E_\delta = \Delta E_\epsilon = \frac{32}{45}d_{1n} - \frac{16}{15}d_{2n}, \quad (2.2c)$$

where the subscripts $\alpha, \beta, \gamma, \delta$, and ϵ refer to the five d orbitals of symmetry $r^2 - 3z^2$, $x^2 - y^2$, xy , yz , and zx , respectively. The values of d_{1n} and d_{2n} , which are the contributions to the energy shifts from each of the first and second neighbors, are determined by the bulk crystal-field analysis and the assumption^{15,16}

$$d_{2n}/d_{1n} = (dd\sigma)_2 / (dd\sigma)_1, \quad (2.3)$$

where $(dd\sigma)_1$ and $(dd\sigma)_2$ are Slater-Koster tight-binding parameters. Now the position of the d levels of the Fe thin-film structure can be easily obtained. They are listed together with the other Hamiltonian parameters in Table I. It should be pointed out that the crystal-field calculations are carried out so as to keep the center of gravity of the d manifold constant. The large change relative to the bulk value found for the $x^2 - y^2$ orbital is, in fact, caused by a consistent change by the other four orbitals and the large resulting motion of the center of gravity.

Since metallic Fe has a magnetic moment of $2.22\mu_B/\text{atom}$,²⁸ 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.

TABLE I. Hamiltonian parameters (energies are in eV below the Fermi level of the 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.

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

In this configuration there is an average of two holes per atom; therefore the maximum possible magnetic moment is $2.00\mu_B$ /atom. 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.

With five d orbitals/atom spin, there are 20 orbitals in the two-atom cluster. Simple combinatorial arguments yield 4845 states for four holes in the cluster. The photoemission process introduces a fifth hole, yielding 15 540 final states. Inverse photoemission removes a hole, leaving three in the cluster, for a total of 1140 final states. 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. 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. For the case of five (three) holes in the cluster, there are 1512 (0) sextets, 7392 (480) quadruplets, and 6600 (660) doublets. 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,¹⁵ of order 8. It possesses five irreducible representations with the following degeneracies: γ_1 ($d=1$), γ_2 ($d=1$), γ_3 ($d=1$), γ_4

($d=1$), and γ_5 ($d=2$). With a complete set of matrices that transform according to these irreducible representations,²⁹ 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 largest blocks for five and three holes in the cluster³⁰ are 820×820 and 82×82 , reduced from the original $15\,540 \times 15\,540$ and 1140×1140 , respectively. The various block sizes are shown in Table II. The solutions obtained by diagonalizing these blocks are exact solutions of the full Hamiltonian for the cluster.

III. PHOTOEMISSION AND INVERSE PHOTOEMISSION

Photoemission and inverse-photoemission measurements provide a useful probe of the electronic structure in many-body systems. The physical process involved is intrinsically short ranged. Therefore, it should be well described in the periodic-small-cluster approach.

The photoemission (inverse-photoemission) process adds (removes) a hole into (from) the system. The one-electron density of emitted (absorbed) states (DOS) is calculated by adding (removing) a hole to (from) the four-hole ground state and projecting the result onto the eigenstates of the cluster with five (three) holes. When a hole of particular spin orientation and spatial symmetry is added (removed), one obtains a spin- and angle-resolved DOS. These may be added together to obtain the total d -band-photoemission (inverse-photoemission) DOS.

For four holes in the cluster the Hamiltonian (2.1) yields a nondegenerate (except spin) ground state of symmetry $^5\gamma_4$. The photoemission spectrum is defined as

$$F_{\text{PE}}(\epsilon, \mu\sigma) = \sum_k |\langle v^{(k)} | c_{\mu\sigma} | \psi_0 \rangle|^2 \delta(\epsilon - \epsilon^{(k)} + \epsilon_0), \quad (3.1)$$

where $|v^{(k)}\rangle$ is the k th eigenstate in the five-hole manifold of the cluster, $|\psi_0\rangle$ is the four-hole ground state, and $\epsilon^{(k)}$ and ϵ_0 are the corresponding eigenvalues. The opera-

TABLE II. 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
$N=3$	$J = \frac{3}{2}$	14	14	14	14	32
	$J = \frac{1}{2}$	41	42	41	42	82
$N=4$	$J=2$	31	27	21	27	52
	$J=1$	117	121	127	121	252
	$J=0$	119	106	94	106	200
$N=5$	$J = \frac{5}{2}$	34	32	34	32	60
	$J = \frac{3}{2}$	230	230	230	230	464
	$J = \frac{1}{2}$	414	416	414	416	820

tor $c_{\mu\sigma}$ destroys an electron, or, equivalently, creates a hole in the four-hole ground state. The subscript μ runs over the 10 d orbitals in the cluster. The quantity

$$G_{\text{PE}}(\varepsilon) = \sum_{\mu, \sigma} F_{\text{PE}}(\varepsilon, \mu\sigma) \quad (3.2)$$

is called the fully integrated photoemission spectrum; the quantity

$$S_{\text{PE}}(\varepsilon, \sigma) = \sum_{\mu} F_{\text{PE}}(\varepsilon, \mu\sigma) \quad (3.3)$$

is called the spin-resolved photoemission spectrum. Those for the inverse-photoemission spectrum are similarly defined as

$$F_{\text{IPE}}(\varepsilon, \mu\sigma) = \sum_k |\langle v^{(k)} | c_{\mu\sigma}^\dagger | \psi_0 \rangle|^2 \delta(\varepsilon - \varepsilon^{(k)} + \varepsilon_0), \quad (3.4)$$

$$G_{\text{IPE}}(\varepsilon) = \sum_{\mu, \sigma} F_{\text{IPE}}(\varepsilon, \mu\sigma), \quad (3.5)$$

$$S_{\text{IPE}}(\varepsilon, \sigma) = \sum_{\mu} F_{\text{IPE}}(\varepsilon, \mu\sigma). \quad (3.6)$$

Figure 2 shows the fully integrated and spin-resolved photoemission spectra $G_{\text{PE}}(\varepsilon)$ and $S_{\text{PE}}(\varepsilon)$. Figure 3 displays $G_{\text{IPE}}(\varepsilon)$. [Note that the ground state of the neutral cluster is a fully saturated ferromagnetic state, i.e., all the holes are in the minority-spin levels.³¹ In the IPE experiment an electron cannot be absorbed unless there is already a hole there. Therefore, one should expect that all the peaks in IPE spectra are of minority-spin character. This is indeed the case of the calculated results. In this case, $G_{\text{IPE}}(\varepsilon)$ and $S_{\text{IPE}}(\varepsilon)$ are the same.] In all the figures the sharp lines characteristic of a finite system have been artificially broadened with Gaussian peaks of 0.1 eV half-width. The units are chosen such that the quantity $\int d\varepsilon G_A(\varepsilon)$ (with A denoting PE or IPE) is equal to the number of the holes in the cluster in IPE and equal to the number of the electrons³² in the cluster in PE. Therefore, in the model defined in this paper, the "arbitrary units" for IPE and PE strength should actually read "0.5 hole/atom eV" and "0.5 electron/atom eV," respectively.

Comparing these results with the bulk results of Ref. 14, one can immediately see³³ some interesting features caused by the presence of the surface. First, there is a pronounced band narrowing in the major part of the PE spectra close to the Fermi level. This is a direct consequence of the reduction of the number of neighbors for

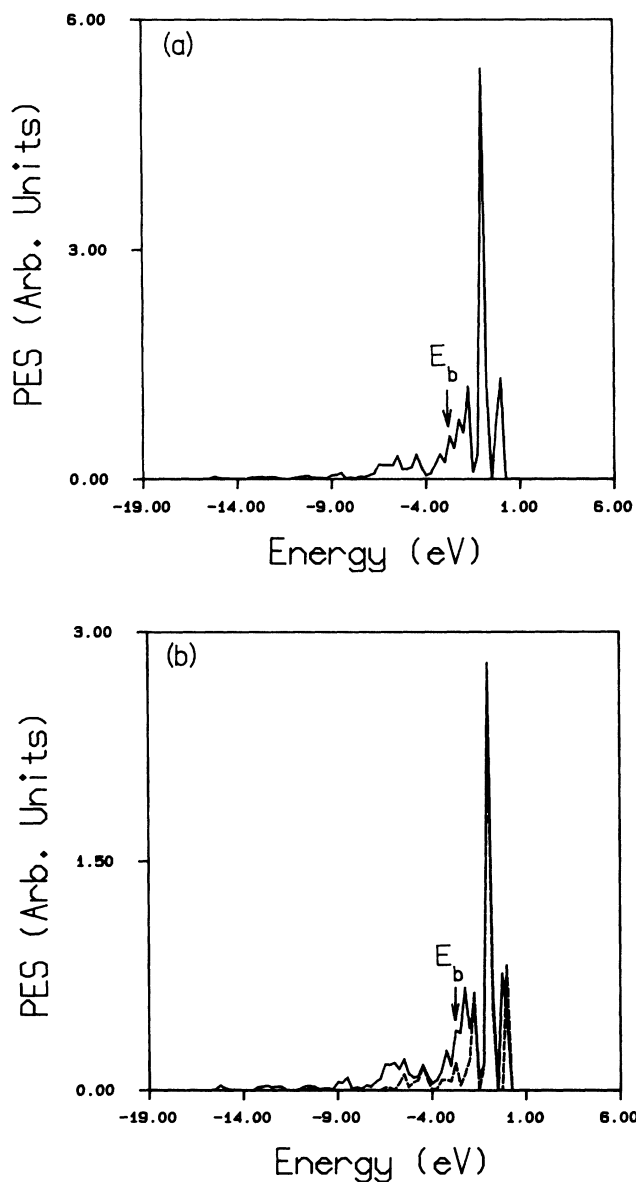


FIG. 2. Total photoemission spectrum (PES). (a) Fully integrated results. (b) Spin-resolved results. Solid lines correspond to the majority-spin states and dashed lines correspond to the minority-spin states. The location of the lowest one-electron state in the d band according to the single-particle calculation is denoted E_b .

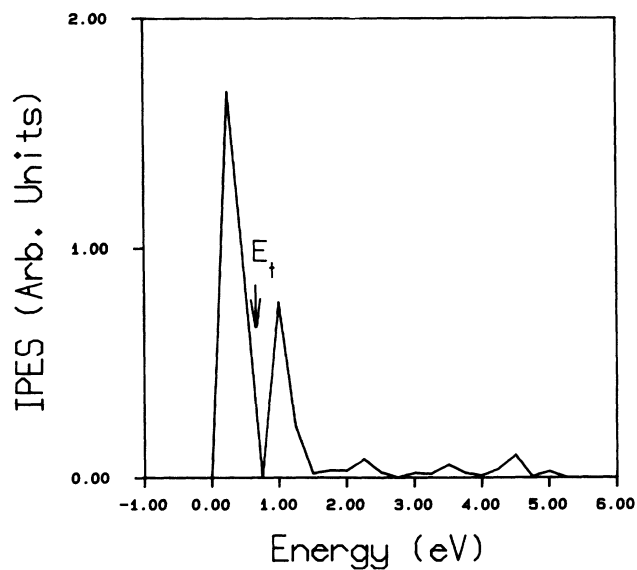


FIG. 3. Total inverse-photoemission spectrum (IPES). The peaks in the spectrum are fully polarized in the minority-spin orientation. The location of the highest one-electron state in the d band according to the single-particle calculation is denoted E_t .

TABLE III. One-particle eigenvalues (energies are in eV below the Fermi level of the bulk Fe metal) for the 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

atoms at surfaces.³⁴ In the IPE spectrum, major peaks are located close to the Fermi level within about 1.5 eV, but the whole range of the spectrum is also reduced by about 3 eV from the bulk result. Another important feature here is that the relative weights of the peaks in the satellite part (i.e., for $E < E_b$ or $E > E_t$, where E_b and E_t are the bottom and top of the d band predicted by the band-theoretical calculations) are larger than those in the bulk case. This is an indication that the many-body correlation effects are stronger in the surface case. This result is consistent with the calculated PE results for the Ni(001) surface¹⁶ and the experimental observations^{35,36} of the magnetization enhancement at Fe and Ni surfaces. Furthermore, it can be seen from the spin-resolved PE spectrum [Fig. 2(b)] that the exchange splitting is fairly small in the “main-line” part (i.e., $E > E_b$) and quite large in the satellite part (i.e., $E < E_b$).

The four-hole ground state $^5\gamma_4$ is fully polarized. This means that the ratio of up- and down-spin states in the ground state should be 10/6. (Remember that there are 10 d orbitals, which can accommodate 20 particles, in the cluster, and the holes in the ground state are all in minority-spin levels.) Therefore, the following sum rule of the relative polarization should hold in the PE calculations,

$$(I_+ - I_-)/(I_+ + I_-) = (10 - 6)/(10 + 6) = 25\% , \quad (3.7)$$

where I_+ and I_- are the total intensities of the majority- and minority-spin states. One interesting feature in the spin-resolved PE spectrum is that the relative spin polarization in the “main-line” part of the spectrum is very small, but the peaks in the satellite part are highly polarized in majority-spin orientation. This can be easily understood in the present model: when holes with majority-spin orientation are introduced into the level where there are already minority-spin holes, they will experience a large Coulomb repulsion (which is not properly treated in local-density-approximation calculations) and eventually end up in the satellite part of the spectrum.

To illustrate in more detail the many-body effects in photoemission and inverse photoemission at the Fe surface, it is instructive to project the density of the emitted and absorbed one-electron states onto the levels of various symmetries. In the bulk Fe case¹⁴ the projected results can be easily qualitatively understood in the one-

particle picture, although in the full many-body approach configuration interaction mixes all one-particle levels and produces quantitative changes. However, the situation is quite different in the Fe-surface case. The calculated one-particle energy levels of the Fe-surface system discussed here are listed in Table III. Projected Fe-surface PE and IPE spectra are shown in Figs. 4 and 5. One can see that the one-particle picture can no longer explain (even qualitatively) some of the major features in the spectra. While a large part of the contributions to the emitted DOS in PE close to the Fermi level comes from the states of symmetries γ_1 , γ_2 , and γ_5 , as expected from the one-particle picture, strong peaks of γ_3 symmetry with both spin orientations appear in the spectrum close to the Fermi level. This is definitely induced by many-body correlation effects. In the IPE spectra large peaks of symmetries γ_3 and γ_4 are observed close to the Fermi level. Again, this result can only be understood in the full many-body approach where all one-particle levels are mixed. These projected PE and IPE spectra distinguish the contributions from states of different symmetries and thus give much detailed information about the many-body electronic structures of the system investigated.

The calculated PE and IPE spectra presented in this section should be compared with surface-sensitive, valence-band, normal-emission PE and IPE experiments with incident-photon energies in a range such that the penetration depth of the photons is about one single atomic layer. Although fine details of true Fe(001)-surface PE and IPE results may be different from what has been obtained here, the general trend and major features should be well described by the present model due to the large contributions from the many-body effects, which are treated exactly in this approach. In particular, it should be easier to observe satellite peaks at the Fe(001) surface because of the larger relative weights in the surface case. Spin-resolved PE measurements should be able to detect the high-spin polarization of the satellite peaks.

IV. CONCLUSIONS

A many-body periodic-small-cluster model of $3d$ electrons for a (001) dilayer of Fe has been studied to explore the modification of the electronic structure in the presence of surfaces. This approach incorporates both band-structure effects and many-body correlations on an equal footing. Although one should not expect that this model will give a good quantitative description of true Fe(001) surface due to the shortcomings of the present model discussed in the Introduction, general trends and major features obtained in this calculation should hold because of the large contributions from the many-body correlation effects, which are treated exactly. This approach presents an exactly solvable model for a highly correlated many-body system; it is quite interesting in its own right. It is straightforward to extend and modify this model to study other highly correlated metals.

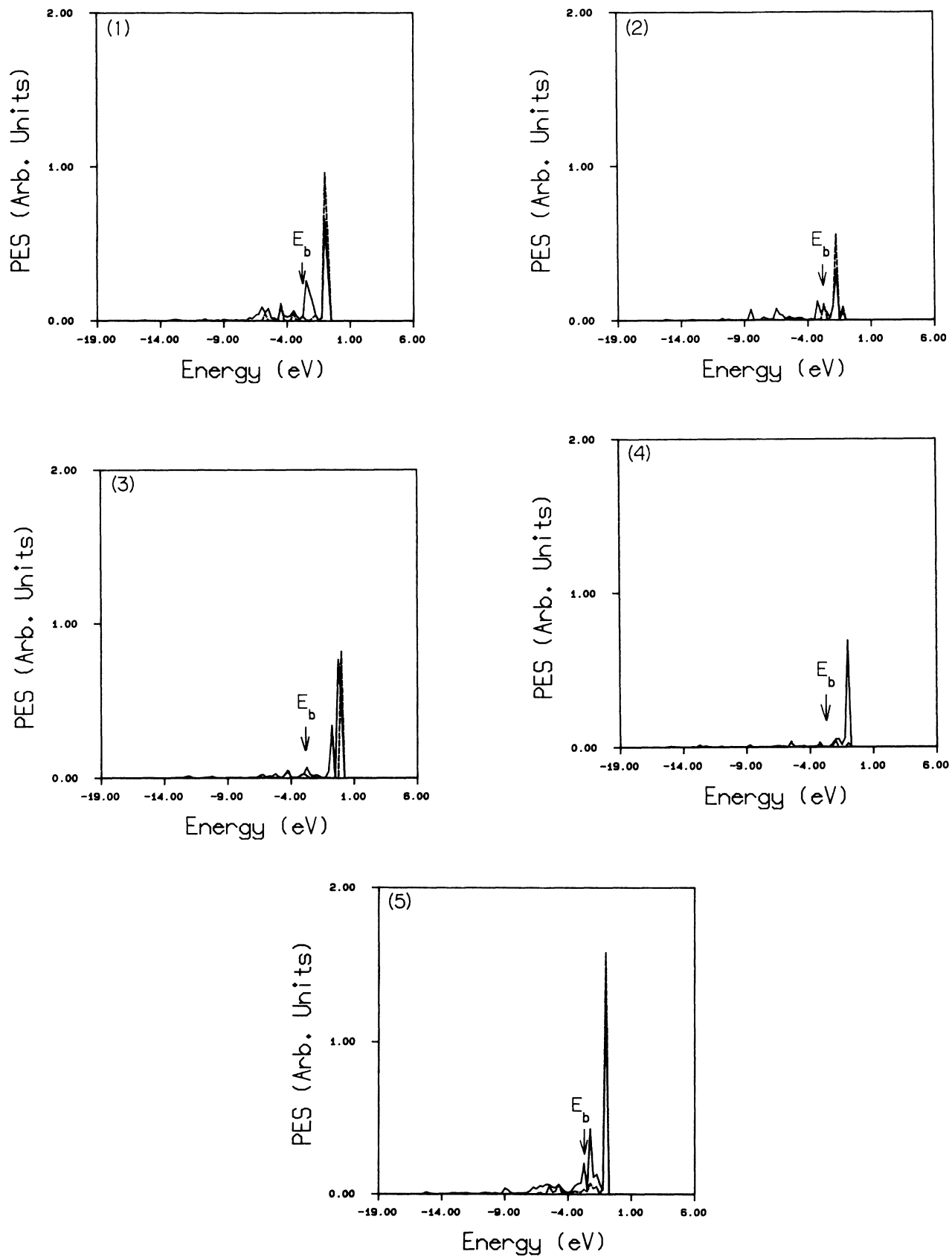


FIG. 4. Spin-resolved projected photoemission spectrum (PES). (1)–(5) correspond to the states of symmetries γ_1 , γ_2 , γ_3 , γ_4 , and γ_5 , respectively.

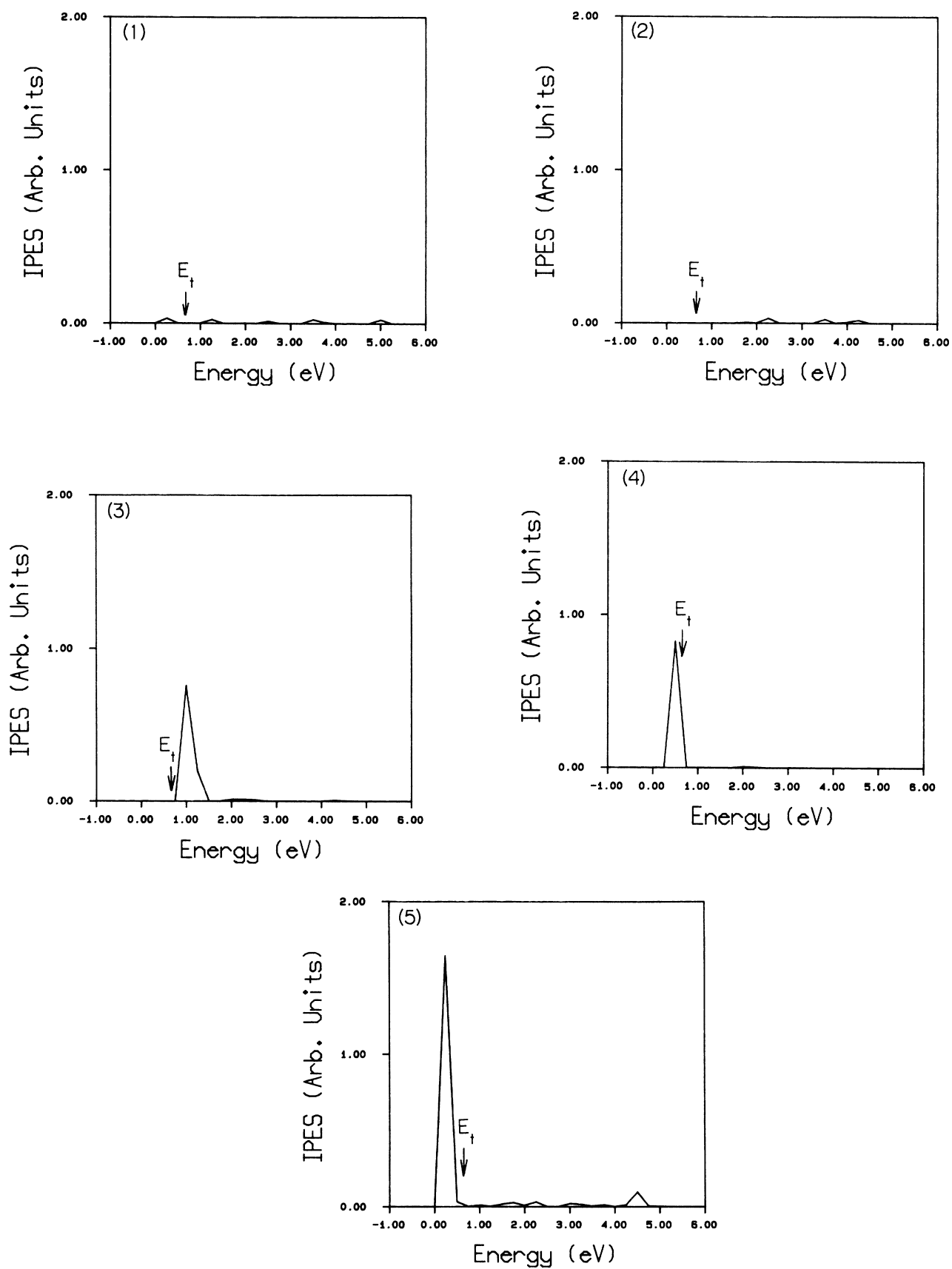


FIG. 5. Spin-resolved projected inverse-photoemission spectrum (IPES). (1)–(5) correspond to the states of symmetries γ_1 , γ_2 , γ_3 , γ_4 , and γ_5 , respectively.

It is found that crystal-field effects and the associated changes in the single-particle electronic structure play an important role in determining the many-body electronic structure at the Fe(001) surface. There is a pronounced band narrowing induced by the appearance of the surface. Photoemission and inverse-photoemission calculations show that many-body correlation effects are stronger in the surface case than those in the bulk bcc Fe. All the one-particle energy levels are strongly mixed by configuration interactions. It is impossible to correctly explain (even qualitatively) some major features in the photoemission and inverse-photoemission spectra in the one-particle picture; a full many-body approach is necessary in understanding the results. The exchange splitting of the states close to the Fermi level in the photoemission spectra is fairly small, but the spin polarization of the satellite peaks is very high. The relative weights of satellite peaks in the spectra are larger than those in the bulk case. This should make it easier to detect the satellite peaks at the Fe(001) surface. Surface-sensitive, valence-

band, normal-emission photoemission and inverse-photoemission experiments are suggested to test the results reported here.

Note added in proof. Recently, a surface-sensitive, normal-emission, spin-polarized photoemission measurement was reported for Fe(001) by N. B. Brookes, A. Clarke, and P. D. Johnson [Phys. Rev. Lett. **63**, 2764 (1989)]. The main features in our calculated photoemission spectra are in fairly good agreement with the experiment. This result shows that the periodic-cluster approach describes the photoemission process in Fe very well, even in an approximate model used in the present work.

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- ¹See, for example, F. J. Himpsel, Adv. Phys. **32**, 1 (1983); Comments Condensed Matter Phys. **12**, 199 (1986).
- ²J. Callaway and C. S. Wang, Phys. Rev. B **16**, 2095 (1977).
- ³K. B. Hathaway, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **31**, 12 (1985).
- ⁴C. S. Wang, R. E. Prange, and V. Korenman, Phys. Rev. B **25**, 5766 (1982).
- ⁵R. A. Tawil and J. Callaway, Phys. Rev. B **7**, 4242 (1973).
- ⁶H. S. Greenside and M. A. Schlüter, Phys. Rev. B **27**, 5 (1983).
- ⁷S. Ohnishi, A. J. Freeman, and M. Weinert, Phys. Rev. B **28**, 6741 (1983).
- ⁸E. M. Haines, V. Heine, and A. Ziegler, J. Phys. F **15**, 661 (1985); **16**, 1343 (1986).
- ⁹K. Lee, J. Callaway, and S. Dhar, Phys. Rev. B **30**, 1724 (1984).
- ¹⁰S. Hüfner and G. K. Wertheim, Phys. Lett. **51A**, 299 (1975); C. Guillot, Y. Ballu, J. Paigne, J. Lecante, K. 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).
- ¹¹D. R. Penn, Phys. Rev. Lett. **42**, 921 (1979); A. Liebsch, *ibid.* **43**, 1431 (1979); N. Mårtensson 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).
- ¹²R. H. Victora and L. M. Falicov, Phys. Rev. Lett. **55**, 1140 (1985).
- ¹³L. M. Falicov, in *Recent Progress in Many-Body Theories*, edited by E. Pajanne and R. Bishop (Plenum, New York, 1988), Vol. I, p. 275.
- ¹⁴E. C. Sowa and L. M. Falicov, Phys. Rev. B **35**, 3765 (1987).
- ¹⁵Changfeng Chen, Phys. Rev. B **41**, 1320 (1990).
- ¹⁶Changfeng Chen and L. M. Falicov, Phys. Rev. B **40**, 3560 (1989).
- ¹⁷L. M. Falicov and R. H. Victora, Phys. Rev. B **30**, 1695 (1984).
- ¹⁸J. C. Parlebas, R. H. Victora, and L. M. Falicov, J. Phys. (Paris) **47**, 1029 (1986).
- ¹⁹A. Reich and L. M. Falicov, Phys. Rev. B **34**, 6752 (1986); **36**, 3117 (1987); **37**, 5560 (1988); **38**, 11 199 (1988).
- ²⁰E. C. Sowa and L. M. Falicov, Phys. Rev. B **37**, 8707 (1988).
- ²¹C. R. Proetto and L. M. Falicov, Phys. Rev. B **38**, 1745 (1988).
- ²²Changfeng Chen, A. Reich, and L. M. Falicov, Phys. Rev. B **38**, 12 823 (1988).
- ²³J. Callaway, D. P. Chen, and R. Tang, Z. Phys. D **3**, 91 (1986); Phys. Rev. B **35**, 3705 (1987).
- ²⁴J. Callaway, Phys. Rev. B **35**, 8723 (1987).
- ²⁵J. Callaway, D. P. Chen, D. G. Kanhere, and P. K. Misra, Phys. Rev. B **38**, 2583 (1988).
- ²⁶J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954); corrected and extended to include higher angular momenta by R. R. Sharma, Phys. Rev. B **19**, 2813 (1979).
- ²⁷M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964).
- ²⁸C. Kittel, *Introduction to Solid State Physics*, 5th ed. (Wiley, New York, 1976), p. 465.
- ²⁹A. W. Luehrmann, Adv. Phys. **17**, 1 (1968).
- ³⁰Since the ground state in the present case is a fully saturated ferromagnetic state ($J=2$), the final state in the photoemission process can only be either $J=\frac{5}{2}$ or $\frac{3}{2}$ states, i.e., $J=\frac{1}{2}$ states never get involved. This means that the largest Hamiltonian matrix one has to deal with here is 464×464 for the states of symmetry $^4\gamma_5$, instead of the 820×820 one of symmetry $^2\gamma_5$.
- ³¹Any use of the words "majority" or "minority" in the context of the spin orientation of an energy level refers to electronic spin, not to 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.

³²The neutral state of the cluster contains four holes; it must also contain 16 electrons. For this reason, the photoemission spectra are more complicated.

³³It should be noted that there are two sets of bulk results reported in Ref. 14. The saturated ferromagnetic state gives the results closer to those in the modified model discussed in Ref. 20; it has the same ground-state magnetization as that in the present model, but this is the result of an artificial shift of the *d*-orbital energies in the bulk environment.

³⁴However, it is not always true that the appearance of surfaces will reduce the bandwidth. In the Ni(001)-surface case re-

ported in Ref. 16, the *d*-band width in the surface case is larger than the bulk value. This is caused by the crystal-field effects which affect four of the five *d* orbitals at the (001) surface of a fcc crystal, such as Ni, and shift them downward from their bulk value, but leave the one of *xy* symmetry unaffected. Therefore there is an increase in the *d*-band width at the Ni(001) surface.

³⁵C. Rau, Comments Solid State Phys. **9**, 177 (1980).

³⁶U. Gradmann, G. Waller, R. Feder, and E. Tamura, J. Magn. Mater. **31-34**, 883 (1983).