Effects of intersite Coulomb interactions on ferromagnetism: Application to Fe, Co, and Ni

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We reanalyze the condition for metallic ferromagnetism in the framework of the tight-binding approximation and investigate the consequences of the intersite Coulomb interactions using the Hartree-Fock approximation. We first consider a nondegenerate s band, we show that the intersite interactions modify the occurrence of ferromagnetism, and we derive a generalized Stoner criterion. We analyze the main effects due to the renormalization of the hopping integrals by the intersite Coulomb interactions. These effects are strongly dependent on the relative values of the intersite electron-electron interactions and on the shape of the density of states as illustrated by a study of cubic crystals which allowed us to establish general trends. We then investigate a realistic spd tight-binding model, including intra (Coulomb and exchange) and intersite charge-charge Coulomb integrals. This model is used to study the electronic structure (band structure, densities of states, magnetic moment) of bulk ferromagnetic $3d$ transition metals Fe(bcc), Co(hcp and fcc), and Ni(fcc). An excellent agreement with local spin-density-functional calculations is obtained for the three metals, in particular concerning the different widths of the majority and minority spin bands. Thus the tight-binding Hartree-Fock model is capable to describe this effect and provides its consistent interpretation.

I. INTRODUCTION

The origin of ferromagnetism in itinerant systems remains one of the open questions in the condensed-matter theory. Even though spin-density-functional theory gives correctly several predictions concerning the stability of ferromagnetism,[1] it is interesting to develop simple models which point out the important physical parameters governing the ferromagnetic instabilities. Ferromagnetism may occur in two ways: either the paramagnetic (PM) state gets unstable against the ferromagnetic (FM) state for particular values of parameters (so-called Stoner instability), or the strongly polarized FM state, in most cases saturated ferromagnetic (SF) state, has the lowest energy beyond some values of electron-electron interactions, but the PM state is still locally stable in a range of parameters.

It is certainly instructive to understand first the possible mechanisms of ferromagnetism in the case of a narrow s band studied in the tight-binding model using the Hartree-Fock approximation (HFA). When only the on-site matrix element U of the Coulomb interaction are taken into account the Stoner instability occurs when U satisfies the well-known Stoner criterion $UN(E_F)>1$, where $N(E_F)$ is the density of states at the Fermi level per spin, and the majority and minority spin bands are rigidly shifted relative to each other. The influence of the two-site matrix elements of the Coulomb interaction has been thoroughly studied in the pioneering work by Hirsch *et al.* already over a decade ago.[2,3] These ideas were further developed and qualitatively new effects were found, both within the HFA, and by going beyond it.[4–8] In particular, Hirsch *et al.*[2–5] have pointed out that the renor-

malization of the hopping integrals resulting from the Hartree-Fock decoupling of the two-body intersite term of the Hamiltonian plays an important role in the occurrence of ferromagnetism by changing the bandwidths of majority and minority spin bands in a different way, thus modifying the Stoner condition. However, Hirsch *et al.*[2–5] have mainly emphasized the effect of exchange integrals and have only considered a constant density of states or that of a linear chain. Indeed, the nondegenerate model with exchange interactions was proposed to provide explanation of certain itinerant systems, such as EuB_6.[9] Obviously, the conclusions that can be drawn from such a model depend critically on the numerical values of the parameters and we expect the classical charge-charge intersite Coulomb interaction V to be larger than the exchange one.[7] Consequently, we have found interesting to revisit this model by considering more realistic relative values of the Coulomb matrix elements first in the case of a constant density of states, then for the densities of states of real cubic lattices. We will see that in this last case the physics of FM instabilities is significantly modified. Therefore a quantitative study of the influence of intersite Coulomb interactions in FM transition metals needs an accurate description of the density of states and realistic interaction parameters.

However ferromagnetism is found usually in systems with degenerate orbitals and since the early work of Hubbard[10] a variety of theoretical attempts have been undertaken to understand to what extent the orbital degeneracy might play an essential role in particular in the ferromagnetism of Fe, Co, and Ni. The dominating point of view at present is that the degeneracy of d orbitals is crucial,[11–13] since local moments

can form[14] and survive above the Curie temperature due to intra-atomic exchange integrals. Here we will investigate the effect of on-site and intersite interactions in degenerate spd bands, considering realistic parameters. It is clear that the most important matrix elements of the Coulomb interaction involved in FM instabilities contain four d orbitals centered on at most two neighboring sites. The relative values of the matrix elements can be inferred from the results of explicit calculations using atomic wave functions. From these calculations[15] it turns out that the largest on-site matrix elements are those introduced already in our previous paper,[16] while the only non-negligible intersite Coulomb interactions are of electrostatic (i.e., charge-charge) type, arising from the interaction between two electrons in orbitals centered at two neighboring sites. As for an s band, the Hartree-Fock decoupling of these latter terms renormalizes the hopping integrals and we will show that they are responsible for the different d bandwidths for up and down spins which are obtained in local spin-density-functional calculations for the $3d$ FM elements (Fe, Co, Ni). Furthermore, the nearest-neighbor distances being very close for the three metals, it is expected that the nearest neighbor Coulomb interactions should not vary significantly from Fe to Co and Ni. It will be seen that, under this assumption, an excellent agreement is found between local spin density and our tight-binding Hartree-Fock (TBHF) calculations for the band structure, the densities of states, as well as the magnetic moment of the three elements.

The paper is organized as follows. We recall (Sec. II) the s band (extended Hubbard Hartree-Fock) model in which all interactions are limited to first nearest neighbors and derive an analytic generalized Stoner criterion, including electrostatic as well as exchange interactions. Then we revisit the simple model of a constant density of states which can be solved analytically,[2,4,5] and we show that the onset of the Stoner instability and the condition of occurrence of saturated ferromagnetism are strongly dependent on the ratio of the two-site electrostatic interaction and exchange interaction. Finally, in order to illustrate the role of the shape of the density of states, we consider the case of three-dimensional lattices: simple (sc), body-centered (bcc) and face-centered (fcc) cubic lattices for reasonable parameters, with particular emphasis on the role played by intersite Coulomb interactions. In Sec. III, the multiband spd TBHF model, already described by Barreteau et al.,[16] is extended by including the electrostatic intersite Coulomb matrix elements, and the determination of the parameters is discussed. This model is finally used in Sec. IV to analyze the band structures of FM transition metals: Fe, Co, and Ni. We will show that the main effects which can be understood within the s band model using some analytic arguments apply also qualitatively to $3d$ transition metals. The paper is concluded in Sec. V.

II. FERROMAGNETISM IN A NONDEGENERATE s BAND

A. The tight-binding Hartree-Fock model

We start from a tight-binding model for an s band and assume that the set of atomic orbitals $\phi_i(r)$ centered at each site i is orthogonal. We consider the same Hamiltonian as

Hirsch[5] with intersite interactions limited to first nearest neighbors which, in the second quantization formalism, can be written

$$H_s = -t \sum_{i,j\neq i,\sigma} a_{i\sigma}^\dagger a_{j\sigma} + \frac{U}{2} \sum_{i,\sigma} n_{i\sigma} n_{i-\sigma}$$

$$+ \frac{V}{2} \sum_{i,j\neq i,\sigma,\sigma'} a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{j\sigma'} a_{i\sigma}$$

$$+ \frac{J}{2} \sum_{i,j\neq i,\sigma,\sigma'} a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{i\sigma'} a_{j\sigma}$$

$$+ \frac{J'}{2} \sum_{i,j\neq i,\sigma} a_{i\sigma}^\dagger a_{i-\sigma}^\dagger a_{j-\sigma} a_{j\sigma}, \tag{1}$$

where $a_{i\sigma}^\dagger$ is the creation operator of an electron with spin σ in the atomic orbital centered at site i, $n_{i\sigma} = a_{i\sigma}^\dagger a_{i\sigma}$, and $-t$ is the hopping integral between nearest neighbors. The Coulomb interactions are described by the leading on-site term $\propto U$, and by the two-site terms: charge-charge interactions $\propto V$, exchange interactions $\propto J$, and the "pair hopping" term $\propto J'$,

$$U = \langle \phi_i(r)\phi_i(r') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_i(r)\phi_i(r') \rangle, \tag{2}$$

$$V = \langle \phi_i(r)\phi_j(r') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_i(r)\phi_j(r') \rangle, \tag{3}$$

$$J = \langle \phi_i(r)\phi_j(r') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_j(r)\phi_i(r') \rangle, \tag{4}$$

$$J' = \langle \phi_i(r)\phi_i(r') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_j(r)\phi_j(r') \rangle. \tag{5}$$

We will consider in most cases the realistic relation $J = J'$, as obtained for real wave functions from Eqs. (4) and (5).

In the HFA the two-body terms are decoupled in the following way:

$$a_\alpha^\dagger a_\beta^\dagger a_\gamma a_\delta = \langle a_\alpha^\dagger a_\delta \rangle a_\beta^\dagger a_\gamma + \langle a_\beta^\dagger a_\gamma \rangle a_\alpha^\dagger \alpha_\delta$$

$$- \langle a_\alpha^\dagger a_\gamma \rangle a_\beta^\dagger a_\delta - \langle a_\beta^\dagger a_\delta \rangle a_\alpha^\dagger a_\gamma$$

$$- \langle a_\alpha^\dagger a_\delta \rangle \langle a_\beta^\dagger a_\gamma \rangle + \langle a_\alpha^\dagger a_\gamma \rangle \langle a_\beta^\dagger a_\delta \rangle, \tag{6}$$

where the indices denote an atomic spin orbital. Note also that the spin conservation implies that any average $\langle a_\alpha^\dagger a_\beta \rangle$ vanishes when α and β have different spins.

Consequently the HFA leads to a one-particle Hamiltonian

$$H_s^{\text{HF}} = -\sum_{i,j\neq i,\sigma} t_\sigma a_{i\sigma}^\dagger a_{j\sigma} + \sum_{i\sigma} \varepsilon_\sigma n_{i\sigma} - E_{dc}, \tag{7}$$

with the following spin-dependent hopping integrals and orbital energies,

$$t_\sigma = t + (V-J)I_\sigma - (J+J')I_{-\sigma}, \tag{8}$$

$$\varepsilon_\sigma = z(V-J)n + (U+zJ)n_{-\sigma}, \tag{9}$$

E_{dc} stands for the double-counting energy terms and z is the number of nearest neighbors. Here we assume that the system consists of equivalent atoms, then the occupation numbers: $n_\sigma = \langle n_{i\sigma} \rangle$ for electrons of spin σ and the total band filling $n = \Sigma_\sigma n_\sigma$ are the same at each site i. In this model $I_\sigma = \langle a_{i\sigma}^\dagger a_{j\sigma} \rangle$ do not depend on the bond and can be easily obtained from the density of states (per atom) $N_\sigma(E)$. Indeed, choosing the origin of energies at the center of gravity of $N_\sigma(E)$, it follows from Eq. (7) that

$$\sum_{nocc} E_{n\sigma} = \int_{-\infty}^{E_{F\sigma}} E N_\sigma(E) dE = -zt_\sigma I_\sigma, \tag{10}$$

where $E_{n\sigma}$ are the eigenenergies for spin σ. Note that $I_\sigma = I(n_\sigma)$ since the renormalization of the hopping integrals leads to a simple energy rescaling of the density of states without changing its shape.

B. Generalized Stoner criterion and condition for saturated ferromagnetism

The magnetic energy as a function of the magnetic moment $m = n_\uparrow - n_\downarrow$:

$$E_{mag}(m) = \langle H_s^{HF}(m) \rangle - \langle H_s^{HF}(0) \rangle, \tag{11}$$

where $\langle H_s^{HF}(m) \rangle$ is the Hartree-Fock energy of a state with magnetic moment m, is easily expressed in terms of the function $I(n_\sigma)$. Let us introduce the following notations:

$$I_\sigma = I(n_\sigma) = I\left(\frac{n+\sigma m}{2}\right), \tag{12}$$

with $\sigma = +1(-1)$ for up(down) spin. Then the magnetic energy per atom is given by

$$\begin{aligned} E_{mag}(m) = 2zt[I_0 - \tfrac{1}{2}(I_\uparrow + I_\downarrow)] - \tfrac{1}{4}(U+zJ)m^2 - \tfrac{1}{2}z(V-J) \\ \times (I_\uparrow^2 + I_\downarrow^2 - 2I_0^2) + z(J+J')(I_\uparrow I_\downarrow - I_0^2), \end{aligned} \tag{13}$$

where I_0 refers to the PM state, i.e., $I_0 = I(n/2)$.

Let us first derive the condition under which the PM state becomes unstable (Stoner instability). This instability is obtained from the Taylor expansion of I_σ for small magnetization m. Substituting this expansion for $I_\uparrow$ and $I_\downarrow$ into Eq. (13) one finds to second order in m:

$$\begin{aligned} E_{mag}(m) = [-zt I_0'' - z(V-J)(I_0'^2 + I_0 I_0'') \\ + z(J+J')(I_0 I_0'' - I_0'^2) - (U+zJ)]\frac{m^2}{4}, \end{aligned} \tag{14}$$

where I_0' and I_0'' are the first and second derivatives of I_σ at $n_\sigma = n/2$. The Stoner instability occurs when the coefficient of m^2 is negative, i.e.,

$$zI_0''[t + (V-2J-J')I_0] + z(V+J')I_0'^2 + U + zJ > 0. \tag{15}$$

From Eq. (8) it is seen that the term between brackets is the hopping integral t_{PM} in the PM state. Using now Eq. (10) it can be shown, with obvious notations, that

$$I_0' = -\frac{E_F}{zt} = -\frac{E_F^{PM}}{zt_{PM}},$$

$$I_0'' = -\frac{1}{ztN(E_F)} = -\frac{1}{zt_{PM}N_{PM}(E_F^{PM})}, \tag{16}$$

where $N_{PM}(E_F^{PM})$ is the density of states per spin in the PM state at the Fermi level E_F^{PM}. Note that in these equations the energies must be referred to the center of gravity of the band. The inequality (15) can be now rewritten as a *generalized Stoner criterion*:

$$U_{eff}N_{PM}(E_F^{PM}) > 1, \tag{17}$$

with

$$U_{eff} = U + zJ + z(V+J')\left(\frac{E_F^{PM}}{zt_{PM}}\right)^2. \tag{18}$$

This generalizes the criterion derived by Hirsch [Eq. (22)] in Ref. 5 for the particular case of a constant density of states. Accordingly, the influence of the intersite exchange integral J is to act in favor of the FM state for any band filling since it increases U_{eff} and decreases the bandwidth of the PM state [see Eq. (8)]. Let us now examine the effect of V and J'. At low and high band fillings the renormalization of the hopping integral in the PM state tends to zero since I_0 vanishes. As a consequence, due to the term proportional to $V+J'$ in U_{eff} the PM state is more easily destabilized for low values of n. Indeed, in this case, the ratio $(E_F^{PM}/zt_{PM})^2$ is close to unity, as the bottom of the band falls at $E = -zt_{PM}$. This is also true when n approaches $n=2$ for simple and body-centered cubic lattices while this tendency is weakened for the face centered cubic lattice since $(E_F^{PM}/zt_{PM})^2 = 1/9$. Around half filling E_F^{PM} is small so that $U_{eff} \simeq U + zJ$ and for realistic values of V (i.e., $V > 2J + J'$) the PM band is broadened. Moreover its width, like I_0, is there at its maximum and increases with V. Consequently, the PM state is less easily destabilized around half filling.

Finally it is also interesting to derive the value of U above which the SF state with moment m_s ($m_s = n$ when $n \leq 1$, $m_s = 2 - n$ when $n \geq 1$) becomes the most stable. This is done simply by looking for the lowest value of U for which the function $E_{mag}(m)$ [Eq. (13)] takes its minimum value at m_s in the domain $[0, m_s]$.

C. The magnetic instabilities for a constant density of states revisited

In order to obtain a physical insight into the mechanism of FM instability in the s band model [Eq. (7)], we discuss first the case of a constant density of states (per spin, with the zero of energy at ε_σ),

$$N_\sigma(E) = \frac{1}{W_\sigma} \quad \text{for} \quad |E| < W_\sigma/2, \tag{19}$$

with $W_\sigma = 2zt_\sigma$ (in the following we assume $z = 6$). Using Eq. (10) it is found that I_σ has a very simple analytical expression

$$I_\sigma = n_\sigma(1 - n_\sigma). \tag{20}$$

Let us first discuss the renormalization of the hopping integrals for a more than half-filled band, as in the late $3d$ transition metals, in the PM phase as well as in the SF phase which becomes stable when U is large enough. It is clear that the majority spin up band is narrower than the minority spin down one and it can be shown easily that the hopping integral found in the PM phase lies always in between the ones for the majority and minority spins in the SF phase, at least in the realistic case[7] where $V > J$. We will see in Sec. III that this holds also qualitatively for Fe, Co, and Ni.

The study of the stability of the PM and FM states can be done analytically for the constant density of states. For this density of states the magnetic energy [Eq.(13)] is a quadratic function of m^2

$$E_{\text{mag}}(m) = \left[A(n) + B\left(\frac{m^2}{4} \right) \right] \frac{m^2}{4}, \tag{21}$$

with, assuming $J = J'$,

$$A(n) = W - U - \tfrac{1}{2}z[V(3n^2 - 6n + 2) - J(n^2 - 2n - 4)], \tag{22}$$

$$B = -z(V - 3J), \tag{23}$$

and $W = 2zt$. For a given value of n, the minimum of $E_{\text{mag}}(m)$ depends on the actual parameters $A(n)$ and B. The PM state is unstable against the FM state when $A(n) < 0$; in the absence of intersite interactions the well-known Stoner criterion for the constant density of states $U > W$ is recovered. In the general case with $V \neq 0$ and $J \neq 0$ the value of U/W above which the PM state becomes unstable depends on n, as seen in Fig. 1(a).

As shown above, the intersite Coulomb interaction V promotes FM states for low numbers of electrons or holes, while around half filling ($0.5 \lesssim n \lesssim 1.5$), it tends to stabilize the PM state. The intersite exchange matrix element J always favors the FM state since $n^2 - 2n - 4 < 0$ when $0 < n < 2$.

If $A(n) < 0$ and $B > 0$, as considered by Hirsch[5] who assumes $J > V$, the PM state is unstable, and $E_{\text{mag}}(m)$ has a minimum at m_m. If $m_m < m_s$ the most stable solution is a nonsaturated FM state. In this case the condition $dE_{\text{mag}}(m)/dm = 0$, with E_{mag} given in Eq. (21), is equivalent to the condition of equal Fermi energies for the majority and minority spin sub-bands considered instead in Ref. 5. If $m_m > m_s$, the most stable solution is the SF state.

However, for realistic V and J parameters[7,15] one has $V > 3J$, thus B is negative. In this condition if $A(n) > 0$ $E_{\text{mag}}(m)$ has a minimum at $m = 0$, a maximum at m_M and vanishes at $m = m_0$. When $m_0 > m_s$ the PM state is stable and when $m_0 < m_s$ the SF state is the most stable solution but the PM state is metastable. If $A(n) < 0$ the PM state becomes
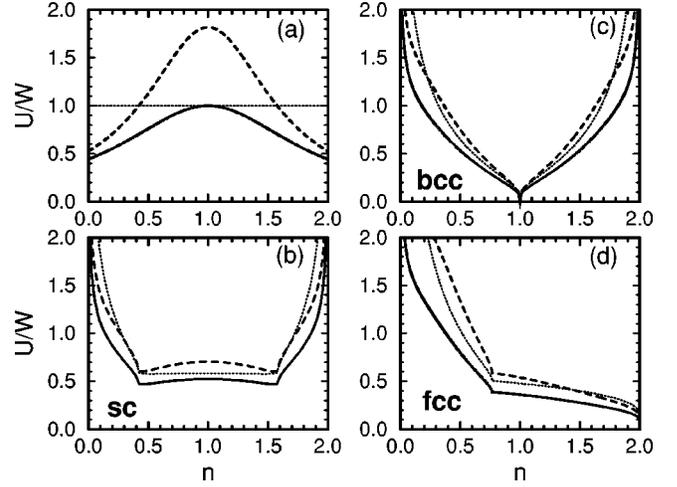

FIG. 1. Critical value of U/W (W: unrenormalized bandwidth) for the onset of the Stoner instability as a function of the band filling n for an s band and: (a) constant density of states, (b) sc lattice, (c) bcc lattice, and (d) fcc lattice. Different lines correspond to: $V = J = 0$ (dotted lines); $V = 0.15U$, $J = 0$ (dashed lines); $V = 0.15U$, $J = 0.03U$ ($J' = J$) (solid lines).

unstable while the SF state remains the most stable solution. Thus if $B < 0$ weak FM states are rigorously excluded and, as U/W increases, the SF state is stable before the Stoner instability of the PM state. The critical value of U/W above which the SF state becomes stable is given by

$$A(n) + \tfrac{1}{4}Bm_s^2 = 0. \tag{24}$$

The variation with n of this critical value is shown in Fig. 2 for the same set of parameters as in Fig. 1(a), and it can be verified that these curves are always *below* the corresponding ones for the Stoner instability, except at $n = 0$ and $n = 2$ where the values of U/W are the same.
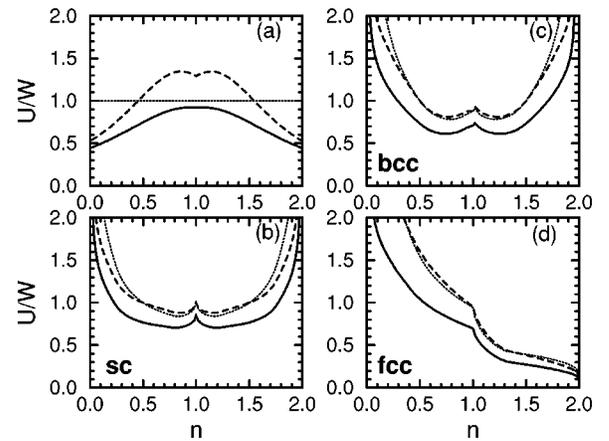

FIG. 2. Critical value of U/W (W: unrenormalized bandwidth) above which the SF phase becomes stable as a function of the band filling n and for: (a) constant density of states, (b) sc lattice, (c) bcc lattice, and (d) fcc lattice. The meaning of different lines and the parameters are the same as in Fig. 1.
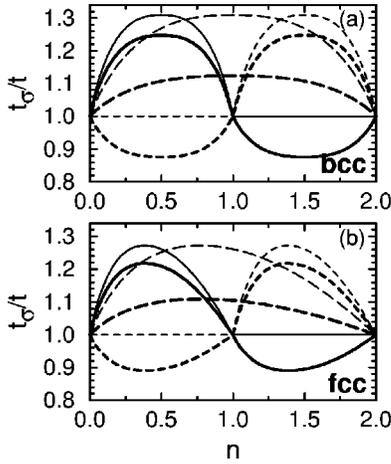
FIG. 3. Effective hopping integrals t_σ (in units of t) as a function of the band filling n of an s band for: (a) bcc and (b) fcc lattices. Different lines refer to: PM phase (long dashed lines), $t_\uparrow/t$ (full lines), and $t_\downarrow/t$ (dashed lines) in the SF phase (stable at sufficiently large U, see Fig. 2). The parameters are: $V=0.15W$ ($W=16t$), $J'=J$, and: $J=0$ (thin lines), $J=0.03W$ (heavy lines).

D. Magnetic instabilities in cubic lattices

In the preceding section we have discussed the FM instability for an s band assuming a constant density of states. However this density of states cannot be associated with any existing lattice. We now consider the case of cubic lattices: simple, body-centered, and face-centered cubic lattices with a hopping integral $-\beta$ limited to nearest neighbors. The corresponding dispersion relation is then

$$E(\mathbf{k})=-\beta\sum_j \exp(i\mathbf{k}\cdot\mathbf{R}_j), \qquad (25)$$

where $\mathbf{R}_j$ ($j=1,\ldots,z$) denote the set of vectors connecting an atom to its nearest neighbors. In this case the density of states, and consequently $I(n_\sigma)$, must be calculated numerically. The densities of states have been obtained from this dispersion relation by carrying out the summation over the Brillouin zone using the linear tetrahedron method.[17]

However, in order to account accurately for the singularities of $N(E)$ we have also used the analytical expressions given by Jelitto[18] which approximate the actual densities of states with an excellent relative error (less than 10^{-4}). The function $I(n_\sigma)$ is derived from Eq. (10) and its derivatives $I'(n_\sigma)$ and $I''(n_\sigma)$, which are necessary to study the Stoner instability [Eq. (15)] are determined by means of the relations (16). In the following we will always assume $J=J'$ and $V>3J$.

The effective hopping integral in the PM state t_{PM} has a maximum at $n=1$ for the sc and bcc lattices, for which $N(E)$ has a particle-hole symmetry, while the maximum is shifted to $n\simeq0.76$ in the case of fcc lattice having asymmetric $N(E)$ (see Fig. 3). In all cases, the effective hopping integral is reduced by $J>0$. At different filling of spin subbands, as for instance in SF states, the effective up- and down-spin hopping elements and the corresponding bandwidths are different. For instance, for $n<1$ the up-spin band-
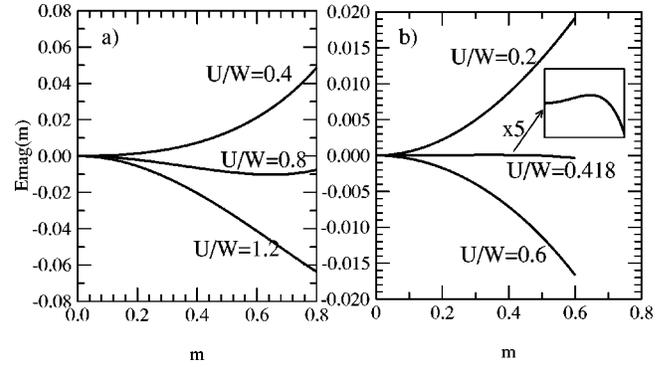

FIG. 4. Magnetic energy E_{mag} (in units of the unrenormalized bandwidth W) as a function of the magnetic moment m for an fcc lattice with an s band for two band fillings (a) $n=0.9$, (b) $n=1.4$, and increasing values of U/W. The other parameters are $V=0.15U$, $J=J'=0$. The inset shows the case $n=1.4$, $U/W=0.418$ with an enlarged energy scale, proving that the PM state is metastable.

width increases when this sub-band is gradually filled, has a maximum at $n\simeq0.38$ for the fcc lattice, and then decreases back to the unrenormalized value at $n=1$, while the down-spin sub-band is unrenormalized (narrowed) when $J=0$ ($J>0$), as shown in Fig. 3(b). The renormalization of spin sub-bands is interchanged for $n>1$ when the up-spin sub-band is filled and thus weakly narrowed in the SF states.

To illustrate the general trends we have determined the Stoner instabilities for sc, bcc, and fcc lattices using Eq. (15), and for three sets of parameters: (i) $V=J=0$, (ii) $V=0.15U$, $J=0$, and (iii) $V=0.15U$, $J=0.03U$. The results are given in Fig. 1 and are in perfect agreement with the qualitative predictions derived above (see Sec. II B). Indeed, V tends to stabilize the FM state for low and high band fillings, while the reverse is found around half filling. Moreover, when J is taken into account, it acts in favor of FM states for any band filling. This result confirms the earlier findings of Hirsch.[2,5]

The regions of stability of the SF phase are shown in Fig. 2. When n approaches 0 or 2 the curves of Figs. 1 and 2 corresponding to the same values of V and J become closer and closer to each other since the magnetic moment is infinitesimal in both limits and the second order expansion of I_σ is valid for any value of $m\leq m_s$. Furthermore, it is found that for all lattices and band fillings, except for the fcc lattice with $n\gtrsim1.3$, the Stoner instability is found for a smaller value of U/W than that needed to stabilize the SF state. This means that, contrary to the case of the constant density of states, the PM state is never metastable except for the fcc lattice with $n\gtrsim1.3$ where a very narrow domain of metastability exists. This is illustrated for the fcc lattice in Fig. 4 where we have plotted $E_{mag}(m)$ for several values of U/W ($V=0.15U$, $J=J'=0$) and two values of the band filling: $n=0.9$ and 1.4. It is clearly seen that, when $n=0.9$, as U/W increases the most stable phase is successively the PM, unsaturated FM and SF phase while, when $n=1.4$, the PM phase is immediately followed by the SF phase but there is a narrow range of U/W where the PM phase is metastable.
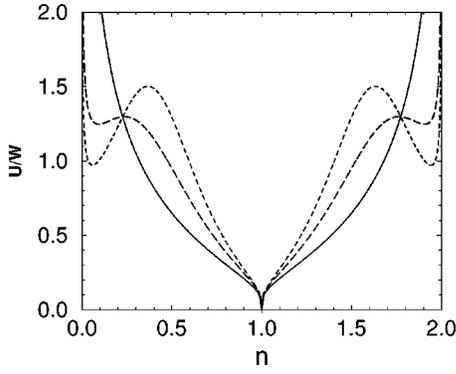
It is important to realize that the above results were de-

FIG. 5. Critical value of U/W (W: unrenormalized bandwidth) for the onset of the Stoner instability in a bcc lattice with an s band as a function of the band filling n for increasing values of V/U (0: full line, 0.35: dashed line, 0.55: dotted line) and $J=J'=0$.

rived using a rather small value of V/U and, consequently, the effect of V is also small. However, it increases rapidly with V as shown in Fig. 5 for the Stoner instability in the fcc lattice. Note that the onset of the Stoner instability is independent of V for two band fillings since, as seen in Eq. (14), E_{mag} does not depend on V when $I'^2_0 + I_0 I''_0 = 0$.

Finally, we must emphasize that all our results discussed so far have been obtained assuming interactions limited to first nearest neighbors. When hopping integrals between farther neighbors are taken into account, the study of the influence of interatomic Coulomb integrals on the electronic structure becomes more involved. Indeed, whereas in the first nearest neighbor case the I_σ function in Eq. (8) can be calculated once for all since the density of states $N(E)$ scales with the hopping integral without changing its shape, this is no longer true when farther neighbor interactions are included and the solution of the problem becomes more tricky. Thus we have carried it out only in the study of the realistic valence spd band of transition metals presented in the following section.

III. FERROMAGNETISM FOR HYBRIDIZED spd BANDS

In the preceding section we presented the effect of interatomic Coulomb interactions on the electronic structure and their influence on the onset of ferromagnetism in a tight-binding s band with interactions limited to first nearest neighbors. From this study we can draw several conclusions. First, the relative numerical values of the parameters are critical to determine the FM instabilities. Then the shape of the density of states has also a strong influence. Thus in order to derive reliable conclusions for FM transition metals we must now generalize this model to hybridized s, p, and d bands with farther interactions as well as realistic Coulomb matrix elements.

A. The Hamiltonian

In the basis of real s, p, and d atomic orbitals (denoted by λ and μ indices) the Hamiltonian is determined by the bare atomic levels ε_λ, the bare hopping integrals $-t_{i\lambda,j\mu}$, and by the matrix elements of the Coulomb interaction. In

the following we keep the most important of these latter terms which can be selected by comparing the numerical values of all the Coulomb matrix elements obtained using explicit expressions of the s, p, and d atomic orbitals. From these calculations,[15] it turns out that the leading intra-atomic Coulomb matrix elements are

$$U_{\lambda\mu} = \langle \phi_{i\lambda}(\mathbf{r})\phi_{i\mu}(\mathbf{r}') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_{i\lambda}(\mathbf{r})\phi_{i\mu}(\mathbf{r}') \rangle, \quad (26)$$

$$J_{\lambda\mu} = \langle \phi_{i\lambda}(\mathbf{r})\phi_{i\mu}(\mathbf{r}') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_{i\mu}(\mathbf{r})\phi_{i\lambda}(\mathbf{r}') \rangle, \quad (27)$$

i.e., the intra-atomic Coulomb and exchange integrals involving two orbitals that we already introduced in a previous paper.[16] These parameters satisfy an important relation for any pair of orbitals with the same orbital quantum number l:

$$U_{\lambda\lambda} = U_{\lambda\mu} + 2J_{\lambda\mu}. \quad (28)$$

Note also that all $U_{\lambda\lambda}$ elements are equal for orbitals λ with the same l. In what follows we consider six Coulomb integrals: U_{ss}, U_{sp}, U_{sd}, $U_{pp'}$, U_{pd}, $U_{dd'}$, and five exchange integrals: J_{sp}, J_{sd}, $J_{pp'}$, J_{pd}, $J_{dd'}$, with $p' \neq p$ and $d' \neq d$, i.e., we have taken the average value of some sets of Coulomb integrals; for instance, $U_{dd'}$ is the average of all Coulomb integrals involving two different d orbitals. The corresponding values of U_{pp} and U_{dd} are determined from Eq. (28).

The most important Coulomb interatomic interactions are:

$$V_{ij}^{\lambda\mu} = \langle \phi_{i\lambda}(\mathbf{r})\phi_{j\mu}(\mathbf{r}') | \frac{1}{|\mathbf{r}-\mathbf{r}'|} | \phi_{i\lambda}(\mathbf{r})\phi_{j\mu}(\mathbf{r}') \rangle, \quad (29)$$

i.e., the electrostatic intersite interactions. From atomic-orbital calculations,[15] it is found that their bare value (before screening) is almost independent of the considered pair of orbitals and close to e^2/R_{ij}, R_{ij} being the spacing between atoms i and j, so that we can approximate them by

$$V_{ij} = V_0 \frac{R_0}{R_{ij}}, \quad \forall \; R < R_c, \quad (30)$$

where R_0 is a reference distance which is chosen to be the first nearest-neighbor bulk equilibrium spacing, V_0 is a parameter to be determined in order to take screening effects into account, and R_c a cutoff distance. We must stress that in this calculation the other two-site matrix elements involving four d orbitals (which are the most important in this problem), and in particular the exchange integrals, are at least two orders of magnitude smaller than V_{ij}.

The spd band Hamiltonian is then written as follows:

$$H = -\sum_{\substack{i\lambda,j\mu,\sigma \\ i \neq j}} t_{i\lambda,j\mu} a^{\dagger}_{i\lambda\sigma} a_{j\mu\sigma} + \sum_{i\lambda\sigma} \varepsilon_{\lambda} n_{i\lambda\sigma} + \sum_{i\lambda} U_{\lambda\lambda} n_{i\lambda\uparrow} n_{i\lambda\downarrow}$$

$$+ \frac{1}{2} \sum_{\substack{i\lambda\mu,\lambda\neq\mu \\ \sigma\sigma'}} U_{\lambda\mu} n_{i\lambda\sigma} n_{i\mu\sigma'}$$

$$+ \frac{1}{2} \sum_{\substack{i\lambda\mu,\lambda\neq\mu \\ \sigma\sigma'}} J_{\lambda\mu} a^{\dagger}_{i\lambda\sigma} a^{\dagger}_{i\mu\sigma'} a_{i\lambda\sigma'} a_{i\mu\sigma}$$

$$+ \frac{1}{2} \sum_{\substack{i\lambda\mu,\lambda\neq\mu \\ \sigma}} J_{\lambda\mu} a^{\dagger}_{i\lambda\sigma} a^{\dagger}_{i\lambda-\sigma} a_{i\mu-\sigma} a_{i\mu\sigma}$$

$$+ \frac{1}{2} \sum_{\substack{ij\lambda\mu,i\neq j \\ \sigma\sigma'}} V_{ij} a^{\dagger}_{i\lambda\sigma} a^{\dagger}_{j\mu\sigma'} a_{j\mu\sigma'} a_{i\lambda\sigma}. \qquad (31)$$

$a^{\dagger}_{i\lambda\sigma}$ and $a_{i\lambda\sigma}$ are the creation and annihilation operators of an electron in the spin orbital $|i\lambda\sigma\rangle$; $n_{i\lambda\sigma}$ is the corresponding occupation number operator. The above multiband Hubbard Hamiltonian can be solved in the framework of the HFA [Eq. (6)] which leads to a one particle TBHF Hamiltonian

$$H_{HF} = \sum_{i\lambda\sigma} \varepsilon_{i\lambda\sigma} n_{i\lambda\sigma} + \sum_{\substack{i\lambda\mu,\lambda\neq\mu \\ \sigma}} h_{i\lambda,i\mu,\sigma} a^{\dagger}_{i\lambda\sigma} a_{i\mu\sigma}$$

$$- \sum_{\substack{i\lambda j\mu\sigma \\ i\neq j}} t_{i\lambda,j\mu\sigma} a^{\dagger}_{i\lambda\sigma} a_{j\mu\sigma} - E_{dc}, \qquad (32)$$

which is the direct generalization of Eq. (7) except for the appearance of new terms $h_{i\lambda,i\mu,\sigma}$, i.e., on-site but interorbital hopping integrals. The latter terms vanish in the bulk for cubic symmetry, and also in hexagonal symmetry except for small sp contributions, but they should be taken into account when the symmetry is reduced.[19] The renormalized matrix elements are given by

$$\varepsilon_{i\lambda\sigma} = \varepsilon_{\lambda} + U_{\lambda\lambda} \langle n_{i\lambda-\sigma} \rangle + \sum_{\substack{\mu\neq\lambda \\ \sigma'}} U_{\lambda\mu} \langle n_{i\mu\sigma'} \rangle$$

$$- \sum_{\mu\neq\lambda} J_{\lambda\mu} \langle n_{i\mu\sigma} \rangle + \sum_{j} V_{ij} \langle n_j \rangle, \qquad (33)$$

$$h_{i\lambda,i\mu\sigma} = -U_{\lambda\mu} \langle a^{\dagger}_{i\mu\sigma} a_{i\lambda\sigma} \rangle + J_{\lambda\mu} (\langle a^{\dagger}_{i\mu\sigma} a_{i\lambda\sigma} \rangle$$

$$+ 2 \langle a^{\dagger}_{i\mu-\sigma} a_{i\lambda-\sigma} \rangle), \qquad (34)$$

$$t_{i\lambda,j\mu\sigma} = t_{i\lambda,j\mu} + V_{ij} \langle a^{\dagger}_{j\mu\sigma} a_{i\lambda\sigma} \rangle. \qquad (35)$$

Note that there is a renormalization of on-site levels due to the charge interaction V_{ij}, but in an homogeneous system where each site has the same charge $\langle n_j \rangle = n$, it simply produces a rigid shift of the levels and can therefore be ignored for bulk calculations. Actually the most important effect of V_{ij} is the renormalization of hopping integrals [Eq. (35)], and thus of the bandwidth, which is different for up and down spins in the FM case.

B. The parametrization of the TBHF Hamiltonian

In order to perform realistic calculations for the FM $3d$ transition metals, we combined the tight-binding approach of Mehl and Papaconstantopoulos[20] for the PM state with corrections originating from the electron-electron interactions in the FM states. At this point, it is important to note that for any bulk geometrical configuration the HF renormalization of the energy levels and of the hopping integrals in the PM state are implicitly included in the parameters of Mehl and Papaconstantopoulos.[20] Indeed, these parameters have been fitted on electronic structure calculations carried out in the density-functional formalism. It is therefore convenient to take the PM state as a reference. The Hamiltonian H can then be written in the following way:

$$H = H_0 + \Delta H - \Delta E_{dc}, \qquad (36)$$

where H_0 is the PM Hamiltonian parametrized in Ref. 20 and ΔH is the perturbation due to the onset of ferromagnetism. More details can be found in Ref. 16. Finally, ΔE_{dc} is the variation of double-counting terms between the FM and PM states. Note that this parametrization assumes a nonorthogonal basis set. Consequently $n = \langle n_j \rangle$ is the net population at site j and not the band filling which is given by the gross atomic population as defined in Ref. 21. However, it is this latter population which should be used to calculate the magnetic moment per atom.

The Coulomb ($U_{\lambda\mu}$) and exchange ($J_{\lambda\mu}$) integrals have been determined from their atomic values and then reduced by appropriate screening factors as explained in Ref. 16. It is at present not possible to get a well controlled procedure which would describe the screening of the atomic interactions when atoms build a crystal. Therefore, we introduce two multiplicative screening factors α_U and α_J operating on the U and J atomic values, respectively. It is known that Coulomb interactions are strongly screened, while exchange interactions remain almost unscreened.[22] This is the reason why we have kept the same value of α_J ($\alpha_J = 0.70$) as in Ref. 16. Let us now discuss the values of α_U and V_0. From Sec. II it is clear that the interaction V_{ij} modifies the onset of ferromagnetism and, consequently, α_U and V_0 should be determined in a correlated way. In addition these parameters should not vary significantly between Fe, Co, and Ni which have almost the same interatomic spacing. We will see in Sec. IV that the values $\alpha_U = 0.12$ and $V_0 = 0.5$ eV lead to bulk spin magnetic moments close to the experimental values and to bulk electronic structures (in particular bandwidths and splitting of the two spin sub-bands) in good agreement with local spin-density calculations for the three ferromagnetic $3d$ elements. Note that the resulting values of $U_{\lambda\mu}$ and $J_{\lambda\mu}$ are small (see Table I) as usual in the HFA to simulate the correlation effects and that the ratio $U_{dd}/V_0 \simeq 4$ seems quite reasonable.

IV. APPLICATION TO FERROMAGNETIC TRANSITION METALS

We have performed TBHF calculations on the three FM $3d$ transition metals Fe(bcc), Co(hcp) and Ni(fcc) at their

TABLE I. Coulomb $U_{\lambda\mu}$ and exchange $J_{\lambda\mu}$ on-site integrals (in eV) obtained from an atomic calculation and screened, respectively, by the factors: $\alpha_U = 0.12$ and $\alpha_J = 0.7$. The intraorbital integrals are given by: $U_{pp} = U_{pp'} + 2J_{pp'}$ and $U_{dd} = U_{dd'} + 2J_{dd'}$.

$U_{\lambda\mu}$	Fe	Co	Ni	$J_{\lambda\mu}$	Fe	Co	Ni
U_{ss}	0.263	0.284	0.304				
U_{sp}	0.158	0.170	0.182	J_{sp}	0.184	0.198	0.213
U_{sd}	0.367	0.367	0.417	J_{sd}	0.105	0.104	0.101
$U_{pp'}$	0.158	0.170	0.182	$J_{pp'}$	0.230	0.248	0.266
U_{pd}	0.294	0.294	0.334	J_{pd}	0.084	0.084	0.081
$U_{dd'}$	0.823	0.886	0.950	$J_{dd'}$	0.571	0.595	0.625

experimental equilibrium structure, i.e, $a_{bcc} = 2.87$ Å for Fe(bcc), $a_{hcp} = 2.51$ Å, $c/a_{hcp} = 1.62$ for Co(hcp), and $a_{fcc} = 3.52$ Å for Ni(fcc). The cutoff radius R_c for the interatomic Coulomb interaction was chosen between second and third nearest neighbors.

A. Ferromagnetic states of bcc Fe

As we have shown in Sec. II, the main effect of the Coulomb intersite interaction is to modify the width of the majority spin band with respect to the minority one. To illustrate this effect in the case of Fe we have performed a self-consistent TBHF calculation with and without this interaction, as shown in Fig. 6. It appears very clearly that the bandwidth of the majority spin d electrons is significantly smaller than that of the minority one when the Coulomb interaction is ''switched on.''

The other effect of the Coulomb intersite interaction is to modify the Stoner instability. In particular, it was shown in Sec. II within the analytic treatment of the s band model that V_{ij} tends to play in favor of the destabilization of the PM states for nearly filled bands. Consequently, we expect an increase of the magnetic moment when V_{ij} increases. This can be seen in Fig. 7, where the evolution of the magnetic moment is plotted for different values of V_0 ranging from 0 to 0.75 eV and fixed values of $U_{\lambda\mu}$ corresponding to $\alpha_U = 0.12$. The spin magnetic moment obtained for $V_0 = 0.5$ eV is in very good agreement with the experimental results[23] (see Table II).

Finally, in Figs. 8 and 9 we have compared the densities of states and band structures as obtained from our TBHF calculation with $V_0 = 0.5$ eV and from fully linearized augmented plane wave (FLAPW) calculations in the local spin density approximation (LSDA) using the WIEN code.[24] The agreement is almost perfect proving that the set of intrasite and intersite Coulomb and exchange interactions that we chose, not only reproduces integrated quantities such as the magnetic moment (see Table II), but is also able to describe very accurately the splitting and the change of bandwidth between majority and minority spins (see Table III).

B. Ferromagnetic states of Co

We now present our results for Co (hcp and fcc) keeping the same values for α_U and V_0 as for Fe. The results of our
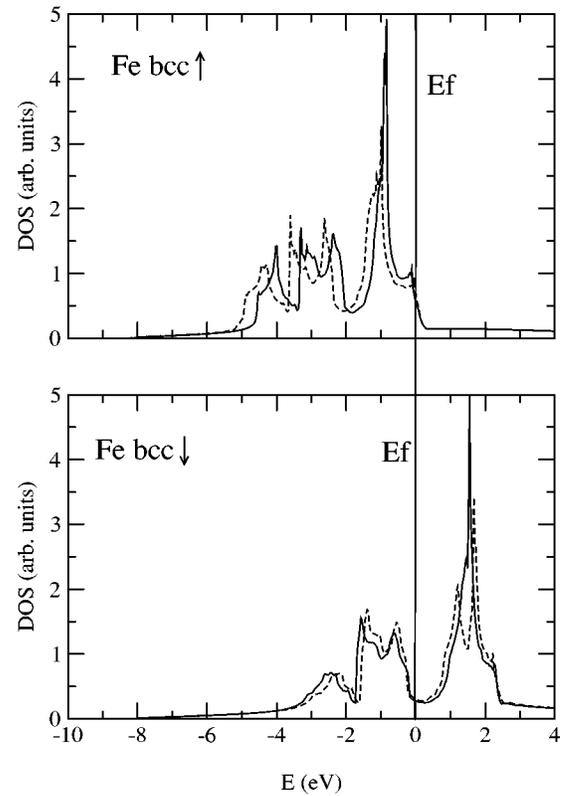

FIG. 6. Density of states as obtained for bcc Fe in the tight-binding Hartree-Fock model with (solid lines, $V_0 = 0.5$ eV) and without (dashed lines) Coulomb intersite interaction, for ↑-spin electrons (top), and ↓-spin electrons (bottom) in the FM ground state.

TBHF and FLAPW LSDA calculations on hcp Co are shown in Fig. 10, where the densities of states obtained with the two methods are represented. Once again the agreement is excellent for the magnetic moment (see Table II) and for the shape and the width of the majority and minority spin densities of states. In particular the difference in bandwidths between majority spin and minority spin d electrons is found to be almost the same as with the WIEN code (see Table III). However, there is a small quasirigid shift of the d band for the
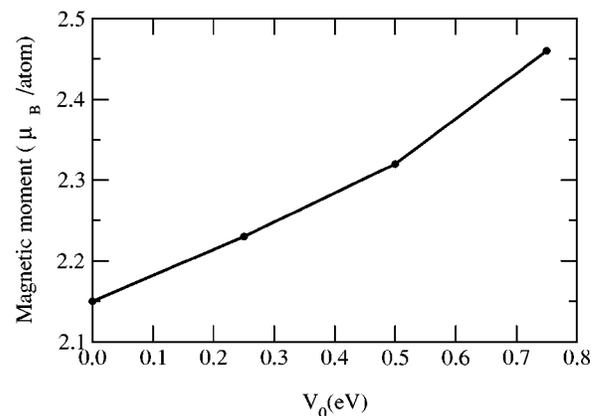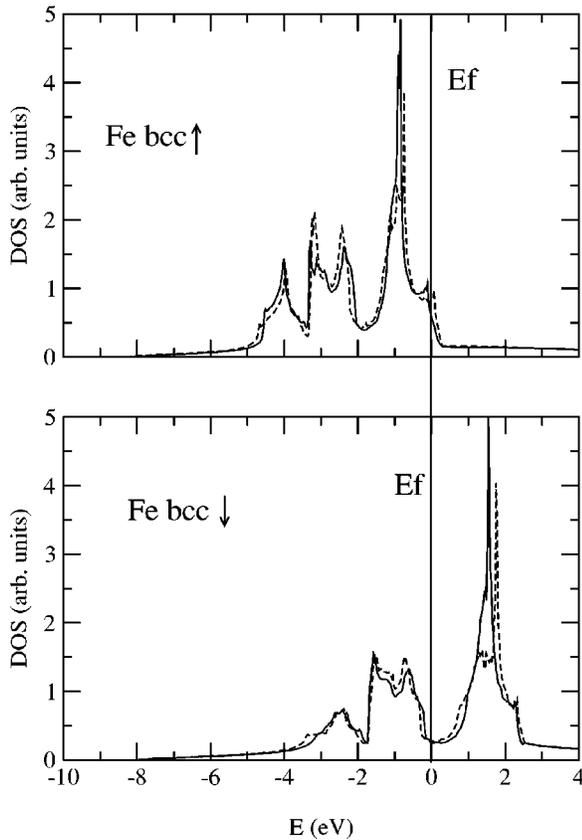

FIG. 7. Variation of the magnetic moment of bcc Fe as a function of the Coulomb intersite interaction V_0.

TABLE II. Comparison of the spin magnetic moments (in Bohr magnetons) obtained from tight-binding Hartree-Fock (TBHF) method, and the WIEN code, compared with experimental values (Ref. 23) for Fe, Co, and Ni.

Element	TBHF	WIEN	Expt.
Fe	2.32	2.23	2.13
Co(hcp)	1.60	1.51	1.57
Co(fcc)	1.59	1.60	–
Ni	0.58	0.58	0.56

majority spin density of states. Note that, Co being a saturated ferromagnet, this small shift has almost no influence both on the magnetic moment and on the total energy. We have also carried out TBHF and FLAPW LSDA calculations on fcc Co with a lattice parameter $a_{fcc} = 3.55$ Å, the densities of states are presented in Fig. 11, showing the same type of agreement between the two methods.

C. Ferromagnetic states of fcc Ni

The same values of α_U and V_0 were also used for Ni. The result is extremely convincing since the magnetic moment is exactly the same with TBHF and the WIEN code (see Table
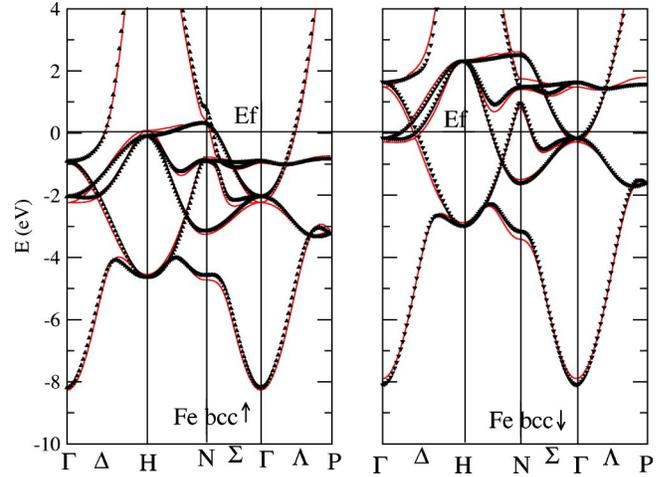

FIG. 9. Electronic structure as obtained for bcc Fe in the tight-binding Hartree-Fock model ($V_0 = 0.5$ eV, black triangles), and in the band structure calculation using the FLAPW method of Ref. 24 (solid lines) for ↑-spin electrons (left), and ↓-spin electrons (right) in the FM ground state.

II), and Fig. 12 shows an excellent agreement for the electronic structure. As for cobalt, there is a slight shift of the majority spin d sub-band without consequences on the magnetic moment and total energy since Ni is also a saturated ferromagnet, but the shape of the densities of states and the changes of the bandwidths (Table III) are very similar.

To conclude this section, the introduction of the intersite Coulomb interaction and the subsequent renormalization of the hopping integrals in the spd TBHF model has enabled us to obtain an excellent overall agreement with calculations based on the density-functional formalism for the band structure, the density of states and the magnetic moment of the three $3d$ FM elements. However the splitting between up- and down-spin bands is systematically slightly larger than in local spin-density calculations. This difference could be expected since with TBHF the self-interaction is forbidden, as it should, while it is allowed in the WIEN code, as usual in the density-functional theory. Indeed, if the self-interaction term is included in Eq. (33), i.e., $\langle n_{i\lambda-\sigma} \rangle$ is replaced by $\langle n_{i\lambda-\sigma} \rangle + \langle n_{i\lambda\sigma} \rangle$, the term proportional to $U_{\lambda\lambda}$ no more contributes to the splitting between up- and down-spin bands.

V. CONCLUSIONS

To summarize, we have used a tight-binding Hartree-Fock model including the renormalization of the hopping integrals due to intersite Coulomb interactions in order to put forward

FIG. 8. Density of states as obtained for bcc Fe in the tight-binding Hartree-Fock model (solid lines, $V_0 = 0.5$ eV), and in the band structure calculation using the FLAPW method of Ref. 24 (dashed lines) for ↑-spin electrons (top), and ↓-spin electrons (bottom) in the FM ground state.

TABLE III. Relative difference in d bandwidths ($W_{d\downarrow} - W_{d\uparrow})/\langle W_d \rangle$, in percentage, as obtained in the TBHF and WIEN code calculations. $\langle W_d \rangle$ is the average bandwidth of both spins.

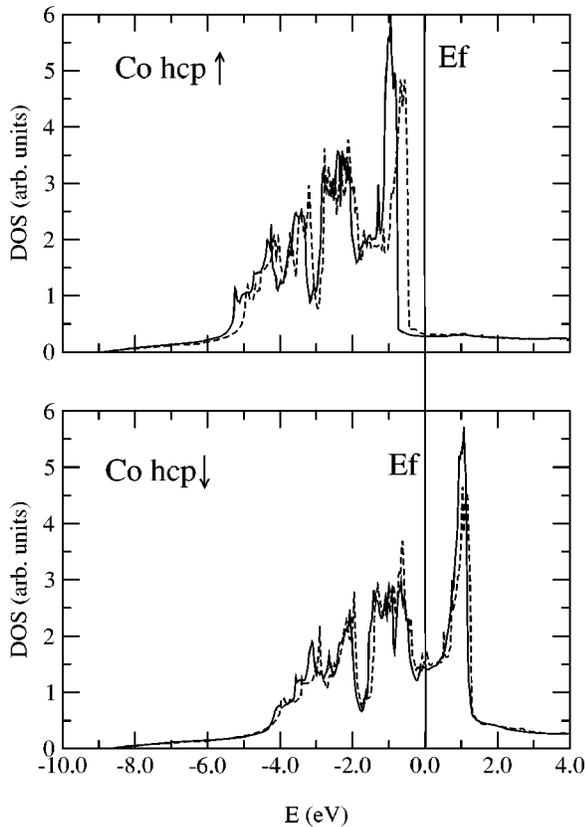| Element	TBHF	WIEN
Fe	15	12
Co(hcp)	16	17
Ni	11	7

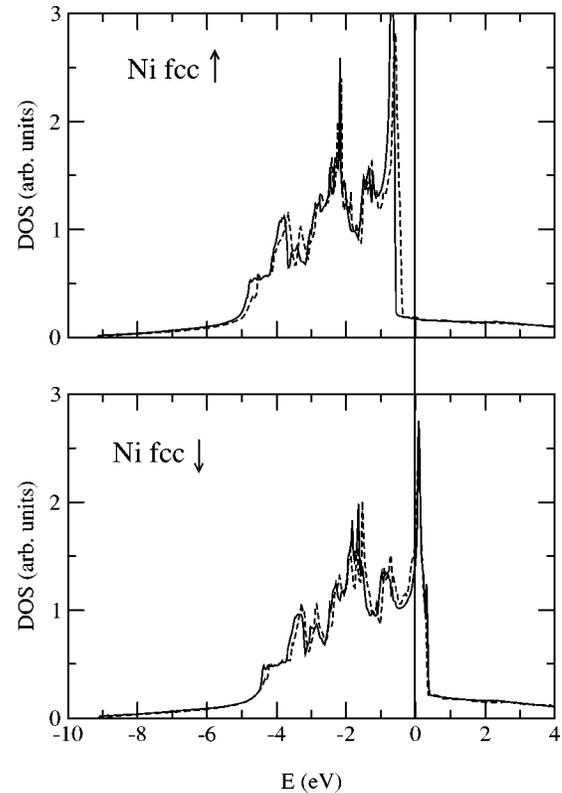FIG. 10. Same caption as in Fig. 8 but for hcp Co.

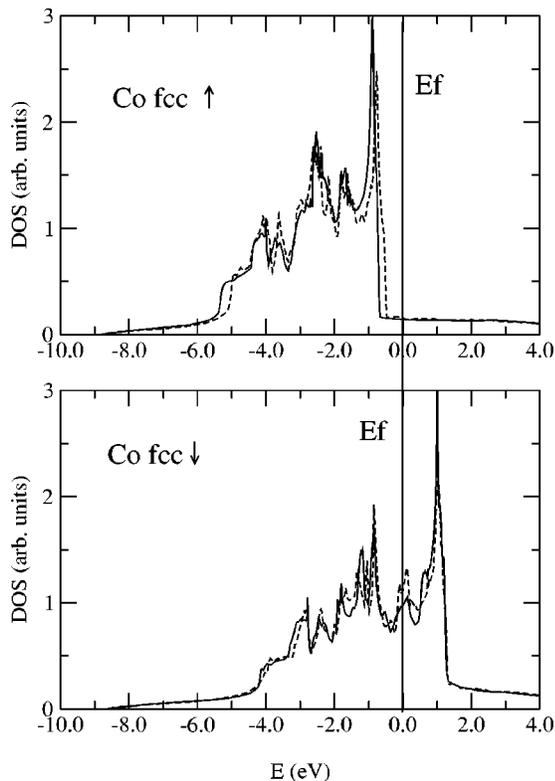FIG. 12. Same caption as in Fig. 8, but for fcc Ni.

FIG. 11. Same caption as in Fig. 8, but for fcc Co.

its influence on the appearance of ferromagnetism. First, we reconsidered the model of a nondegenerate s band and found a generalized Stoner criterion [Eqs. (17) and (18)]. As we have shown, the renormalization of the hopping integrals which originates from the intersite Coulomb elements strongly modifies the conditions for ferromagnetism. In agreement with earlier studies,[2–5] ferromagnetism is favored for nearly filled or empty bands by the nearest-neighbor Coulomb interactions. As the actual FM instabilities are rather sensitive to the system parameters, an accurate description of the density of states and realistic interaction parameters are of crucial importance to understand the behavior of $3d$ transition metals.

Next we have shown that the behavior found for the nondegenerate s band model has important consequences in realistic transition metals. We extended the model to the case of hybridized s, p, and d bands and used it to investigate the electronic structure of FM Fe, Co, and Ni. It was found that the width of the majority spin band is always smaller than that of the minority spin one, as obtained in electronic structure calculations performed by *ab initio* methods. An excellent overall agreement (band structure, densities of states, magnetic moment) with the local spin-density calculations is obtained for the three elements.

Finally, it has to be emphasized that this renormalization of the hopping integrals is also present in the nonmagnetic case and is a function of the environment of the pair of atoms involved in the hopping. Here we have only considered the bulk geometry. It would be interesting to study the case of surfaces and especially of small clusters in which the effect

of the change of environment is expected to be the strongest.

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