Metallic ferromagnetism in a band model: Intra-atomic versus interatomic exchange

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The relative importance of intra-atomic versus interatomic direct exchange in leading to ferromagnetism in metals is not well understood. Here we examine the interplay of these interactions in a tight-binding model with two orbitals per site. The interatomic exchange interaction J is found to always lead to ferromagnetism, and its effect is enhanced by both on-site intraorbital (U) as well as interorbital ($\overline{U}$) Coulomb repulsions. For certain band fillings, and in particular for a quarter-filled band, the intra-atomic exchange interaction J_0 by itself can also lead to ferromagnetism. However, in most cases the magnitude of J_0 required appears to be unphysically large. For other band fillings, J_0 does not lead to ferromagnetism even if infinitely large. In the presence of nearest-neighbor exchange J, J_0 will either enhance or suppress the tendency to ferromagnetism depending on the band filling. These results are used to interpret the occurrence of ferromagnetism in the transition-metal series, and it is concluded that intra-atomic exchange is not likely to play a significant role in the ferromagnetism of Ni or in Ni-Cu and Ni-Zn alloys. Overall our results support the conjecture that intraband interatomic direct exchange is the dominant interaction giving rise to ferromagnetism in metals, and that the essential physics of metallic ferromagnetism is contained in a single-band model without orbital degeneracy. [S0163-1829(97)01241-1]

I. INTRODUCTION

The origin of ferromagnetism in metals is still an unsettled question. While spin-density functional theory (SDFT) can yield first-principles predictions of which materials will exhibit ferromagnetism,[1] it does not provide a simple qualitative physical picture of the origin of metallic ferromagnetism. Obtaining such a picture is important because it would allow to study the phenomenon in much more detail than allowed by SDFT in simple models which, without being realistic, contain the essential physics of the phenomenon. Furthermore, it would allow for broad qualitative prediction regarding the existence of ferromagnetism in either not-yet-existing materials or in materials under extreme conditions of pressure and temperature that have not yet been achieved.

The single-band Hubbard model, with only an on-site repulsion U, was originally introduced as a simple model that may contain the essential physics of the phenomenon.[2] The model exhibits ferromagnetism within the mean-field approximation. However, subsequent work has shown that this model does not display ferromagnetism, except for very special nongeneric cases (e.g., a single hole in a half-filled band[3] or special lattice geometries[4,5]). The degenerate Hubbard model, with two orbitals per site and an intra-atomic exchange interaction has also been studied, particularly for the quarter-filled band case (one electron per site[6–11]). For that case, the model exhibits a coexisting orbitally ordered state and ferromagnetism. However, the orbitally ordered state, being insulating, does not appear to be relevant to the description of metallic ferromagnets. Not much work has been done on the degenerate Hubbard model in other than the orbitally ordered state.

It is in fact widely believed that the existence of band degeneracy is essential to metallic ferromagnetism. This view originated in the work of Slater and co-workers[12,13] and Van Vleck,[14] and is supported by the fact that ferromagnetism in metals has only been found so far in systems that contain atoms with degenerate atomic orbitals (such as d electrons) that can support an atomic magnetic moment through Hund's rule. There is, however, some difficulty in understanding the ferromagnetism of nickel within this framework, whose magnetic moment per atom in the ferromagnetic state is only a fraction of a Bohr magneton, as well as the ferromagnetic state of weak ferromagnets such as Sc_3In, where the constituent atoms are not magnetic.

On the other hand, the possible role of interatomic direct exchange in giving rise to ferromagnetism has been extensively discussed in the past.[15,12,16–18] This mechanism would not require band degeneracy, although the magnitude of the interactions would depend on the nature of the atomic orbitals involved. These studies were invariably framed in the Heitler-London formalism[19] for diatomic molecules. Within that framework, ferromagnetism occurs if the ''Heisenberg J,'' defined as the difference in energy between singlet and triplet Heitler-London states, is positive. The ''Heisenberg J'' is a combination of the Coulomb exchange matrix element and matrix elements of the single-particle potential between nonorthogonal nearest-neighbor orbitals. These studies, notably the very detailed calculations by Stuart and Marshall[17] and by Freeman and Watson,[18] concluded that the Heisenberg J is either negative or positive but very small, and hence that direct exchange cannot be the origin of metallic ferromagnetism.

However, we believe that this conclusion is somewhat misleading, in that it suggests that nearest-neighbor exchange matrix elements are irrelevant to metallic ferromagnetism. It should be kept in mind that these studies were based on the Heitler-London wave function, which is inappropiate for itinerant electrons. We have recently studied the

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effect of nearest-neighbor exchange and pair-hopping processes in an itinerant model, and concluded that they are likely to play a fundamental role in metallic ferromagnetism.[20–22] These matrix elements give rise to ''bond-charge repulsion''[23] and cause a tendency for electrons of opposite spin to occupy states of opposite bonding character to reduce the magnitude of this repulsion, hence favoring ferromagnetism. The possible importance of these matrix elements in tight-binding models and in particular for the understanding of charge-density-wave instabilities was pointed out by Kivelson *et al.*[23] and extensively studied by Campbell and co-workers.[24] Even if small in magnitude we have found that in the presence of strong on-site repulsion these matrix elements, especially nearest-neighbor exchange, give rise to a strong tendency to ferromagnetism. Furthermore, many features of the resulting ferromagnetic state resemble experimental observations.[20] Recently, Vollhardt and co-workers[25] have studied the occurrence of ferromagnetism in generalized Hubbard models using exact techniques and also concluded that nearest-neighbor exchange plays a dominant role.

The purpose of this paper is to examine the combined effect of single-band bond-charge repulsion, i.e., nearest-neighbor exchange and pair hopping, and intra-atomic exchange that arises in the presence of orbital degeneracy. While we believe that the results of Refs. 20–22 and 25 establish that metallic ferromagnetism does generically arise in single-band models, it is in principle possible that the magnitude of the interatomic interactions in real systems is too small to give rise to ferromagnetism and the existence of intra-atomic exchange is essential. Two possible simple scenarios would be either that the main features of metallic ferromagnetism are determined by intra-atomic exchange and bond-charge repulsion plays only a minor role, or conversely, that bond-charge repulsion plays the dominant role and intra-atomic exchange does not qualitatively change the physics. It is also not obvious whether in general interatomic and intra-atomic exchange act cooperatively or whether they can also compete with each other. Nor is it obvious that intra-atomic exchange can always give rise to ferromagnetism in the absence of bond-charge repulsion. In this respect it is of interest to be able to ''turn off'' each of the interactions in turn and consider the effect of the others, which we can do in the model studied. Unfortunately, in nature it is impossible to ''turn off'' the intraband bond-charge repulsion, so that the question whether intra-atomic exchange can give rise to ferromagnetism in the absence of bond-charge repulsion cannot be tested experimentally. On the other hand, in systems where there is no orbital degeneracy one can test whether bond-charge repulsion by itself can give rise to ferromagnetism. One such system is hydrogen at very high densities, where our calculations predict that weak ferromagnetism should set in at temperatures of thousands of degrees.[26]

Among the reasons for the belief that band degeneracy is essential for metallic ferromagnetism, a widely cited one is the result of a detailed calculation by Slater, Statz, and Koster[13] (SSK) for two carriers in nondegenerate and degenerate bands. These workers found that only in the latter case does ferromagnetism occur, and concluded from this that ferromagnetism will never occur in nondegenerate bands. Our results show that this conclusion is flawed for two reasons: (1) ferromagnetic alignment does occur in a nondegenerate band if interatomic interaction matrix elements are included (which were omitted by SSK), and (2) intra-atomic exchange by itself can be totally ineffective in giving rise to ferromagnetism in the degenerate band case when more than two carriers (i.e., one per band) exist.

In the next section we discuss the Hamiltonian being studied and the effect of the various terms in simple limits. In Sec. III we study this model by exact diagonalization of small chains. We conclude with a discussion in Sec. IV.

II. HAMILTONIAN

The Hubbard Hamiltonian for two bands (labeled by $\alpha=1,2$) arising from degenerate orbitals is given by

$$H=H_1+H_2+H_{12}, \tag{1a}$$

$$H_\alpha=-t_\alpha\sum_{\langle ij\rangle,\sigma}(c^\dagger_{i\alpha\sigma}c_{j\alpha\sigma}+\text{H.c.})+U_\alpha\sum_i n_{i\alpha\uparrow}n_{i\alpha\downarrow}, \tag{1b}$$

$$H_{12}=\overline{U}\sum_i n_{i1}n_{i2}+J_0\sum_{i\sigma\sigma'}c^\dagger_{i1\sigma}c^\dagger_{i2\sigma'}c_{i1\sigma'}c_{i2\sigma}+J_0\sum_i(c^\dagger_{i1\uparrow}c^\dagger_{i1\downarrow}c_{i2\downarrow}c_{i2\uparrow}+\text{H.c.}), \tag{1c}$$

where the first term with J_0 describes interband on-site ''exchange'' and the second ''pair hopping'' from one band to the other. U and $\overline{U}$ describe the on-site Coulomb repulsion between electrons in the same and different atomic orbitals, respectively. We have assumed that no hopping between different orbitals at neighboring sites exists. This would be strictly the case if α represented a Wannier rather than atomic orbital, or if such hopping were prevented by symmetry reasons (e.g., hopping in the x direction between orbitals p_y and p_z), and approximate otherwise. We have also assumed that the Wannier functions can be chosen to be real, so that the matrix elements for exchange and pair hopping are the same.

The contribution to this Hamiltonian from intraband bond-charge repulsion is

$$H_{bond}=\sum_{\langle ij\rangle,\alpha}\frac{J_\alpha}{2}\left(\sum_\sigma c^\dagger_{i\alpha\sigma}c_{j\alpha\sigma}+\text{H.c.}\right)^2$$

$$=\sum_{\langle ij\rangle\alpha\sigma\sigma'}J_\alpha c^\dagger_{i\alpha\sigma}c^\dagger_{j\alpha\sigma'}c_{i\alpha\sigma'}c_{j\alpha\sigma}+\sum_{\langle ij\rangle\alpha}J_\alpha(c^\dagger_{i\alpha\uparrow}c^\dagger_{i\alpha\downarrow}c_{j\alpha\downarrow}c_{j\alpha\uparrow}+\text{H.c.}), \tag{2}$$

where the first term is nearest-neighbor exchange and the second is pair hopping. We will assume for simplicity that $t_\alpha = t$, $U_\alpha = U$, and $J_\alpha = J$ are the same for both bands. The interaction matrix elements U, $\overline{U}$, J_0, and J are all positive, and are given by matrix elements of the Coulomb interaction between Wannier orbitals $\varphi_{i\alpha}$ as

$$U = \int d^3r d^3r' \varphi^*_{i\alpha}(r)\varphi^*_{i\alpha}(r')\frac{e^2}{|r-r'|}\varphi_{i\alpha}(r')\varphi_{i\alpha}(r), \tag{3a}$$

$$\overline{U} = \int d^3r d^3r' \varphi^*_{i1}(r)\varphi^*_{i2}(r')\frac{e^2}{|r-r'|}\varphi_{i2}(r')\varphi_{i1}(r), \tag{3b}$$

$$J_0 = \int d^3r d^3r' \varphi^*_{i1}(r)\varphi^*_{i2}(r')\frac{e^2}{|r-r'|}\varphi_{i1}(r')\varphi_{i2}(r), \tag{3c}$$

$$J = \int d^3r d^3r' \varphi^*_{i\alpha}(r)\varphi^*_{j\alpha}(r')\frac{e^2}{|r-r'|}\varphi_{i\alpha}(r')\varphi_{j\alpha}(r), \tag{3d}$$

with i,j nearest-neighbor sites. For large values of the intraorbital on-site repulsion U, as expected to occur in real materials, pair-hopping processes are found to be quantitatively unimportant compared to exchange processes in the calculations described in the next section.

In addition to these interactions there is in principle a variety of other interactions such as interatomic interorbital bond-charge repulsion, interatomic site-site repulsion, and hybrid interactions (site bond), both intra and interatomic. We will not consider these matrix elements here (the role of intersite hybrid matrix elements in ferromagnetism for a single-band model was considered in Ref. 22). If no hybrid intra-atomic matrix elements exist, the interactions U, $\overline{U}$, and J_0 are related by the condition

$$U = \overline{U} + 2J_0, \tag{4}$$

which follows from rotational invariance. In this relation, one of the J_0's on the right-hand side arises from exchange and the other from pair-hopping matrix elements, which we assume to be equal.

The exchange terms can be further decomposed as

$$J_0 \sum_{\sigma\sigma'} c^\dagger_{i1\sigma} c^\dagger_{i2\sigma'} c_{i1\sigma'} c_{i2\sigma} = -J_0 \sum_\sigma n_{i1\sigma} n_{i2\sigma} + J_0 (c^\dagger_{i1\uparrow} c^\dagger_{i2\downarrow} c_{i1\downarrow} c_{i2\uparrow} + \text{H.c.}) \tag{5}$$

and similarly for the interatomic ones. It is clear that the interaction Eq. (5) favors parallel alignment of spins on the same atom, in accordance with Hund's rule, and it is generally assumed that this will also lead to ferromagnetic order if J_0 is sufficiently strong. However, this is by no means obvious, and as we will see in the next section the answer depends on the band filling being considered.

As a simple limiting case that illustrates this point consider the situation where $J_0 \to \infty$, with $\overline{U}$ fixed. In that case, two electrons on the same site form a tightly bound triplet pair, and sites with other occupations are much higher in energy. Hopping of this unit occurs through intermediate states where one electron hops to a neighboring site and the other one follows, with effective amplitude

$$t_{\text{eff}} = \frac{2t^2}{J_0 - \overline{U}} \tag{6}$$

There is furthermore an effective interaction when two of these units with antiparallel spins are at neighboring sites, given by

$$V_{\text{eff}} = -\frac{4t^2}{J_0 + U}, \tag{7}$$

which is attractive, and a hard-core condition that prevents two of these units from being at the same site. Thus the effective model in this subspace is similar to the strong-coupling limit of the single-band Hubbard model (except that there are no three-site terms or exchange of antiparallel spins to lowest order). Although this system may have a pairing instability, there is no tendency for parallel alignment of spins at different sites, except perhaps close to half-filling where Nagaoka's scenario would apply.

On the other hand, the interatomic exchange terms will always favor itinerant ferromagnetism by lowering the kinetic energy of conduction electrons. This was discussed in Ref. 20.

For a quarter-filled band and strong interactions the system becomes insulating and orbitally ordered: electrons occupy alternating orbitals on alternating sites.[6–11] In that case an effective Hamiltonian can be constructed in the subspace of singly occupied sites, describing spin and orbital degrees of freedom. Several studies of this regime have shown that the system orders ferromagnetically.[6–11]

Finally, the mechanism of ''double exchange''[28] will operate in this model when the two bands have different fillings, which would be achieved by including different site energies for the two orbital states. If one of the bands has one electron per site and there is a small carrier concentration (electron or holes) in the other band, the hopping of the carriers is enhanced (in the presence of intra-atomic J_0) when the spins in the other band are aligned, thus favoring ferromagnetic order.[28]

III. RESULTS

We will use units so that $t = 1$. For the one-dimensional chain the bandwidth is $W = 4t$, so that if we assume that $t = 1$ eV it would roughly correspond to bandwidths of transition metals near the end of the transition-metal series.[1] Hence we may loosely think of the values of the dimensionless parameters used in this section to correspond to eV values in real materials. Realistic values of the intraorbital Coulomb repulsion might be $U \sim 10-20$ eV, and of intra-atomic exchange $J_0 \sim 1$-2 eV.[7] The interatomic exchange and pair-hopping parameter J is likely to be a fraction of an eV in real materials (except at very high densities).[26] In the numerical calculations we have not included the intra-atomic pair-hopping

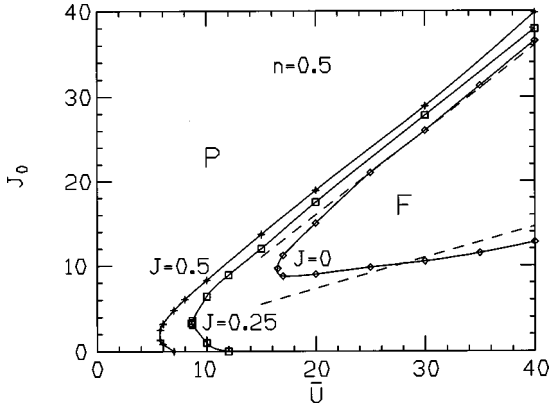

FIG. 1. Phase boundaries in the $\overline{U}$-J_0 plane for a quarter-filled four-site system (two electrons per band). $n=0.5$ indicates the band filling (electrons per band over number of sites). The dashed lines indicate the approximate phase boundaries Eq. (6). Phase boundaries for $J=0$, $J=0.25$, and $J=0.5$ are shown. Here and in the following figures $U=\overline{U}+2J_0$ unless otherwise indicated.

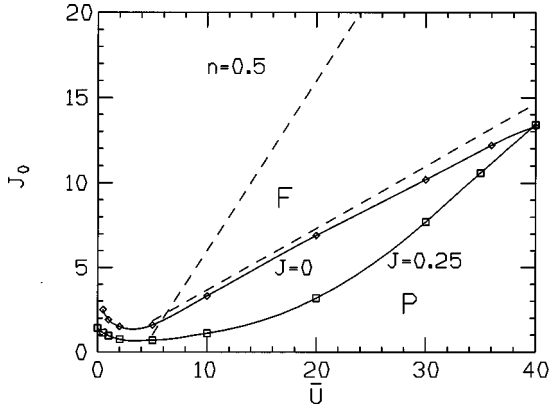

FIG. 2. Same as Fig. 1 for a six-site system with three electrons per band.

term [second term in Eq. (1c)] because it is quantitatively unimportant for realistic values of $\overline{U}$ and significantly increases the size of the Hilbert space. However, we still maintain the relation Eq. (4), obtained assuming that the pair-hopping matrix element is nonzero. This procedure is consistent as the pair-hopping term is not neglected because the matrix element is small, but rather because pair-hopping processes are suppressed for large $\overline{U}$. We will use periodic boundary conditions unless otherwise indicated.

We study the region of stability of the fully polarized ferromagnetic state by comparing the ground-state energy of that state with that of unpolarized as well as partially polarized states. For strong interactions it is generally found that the transition occurs directly from fully polarized to unpolarized, while for weak interactions there is often a parameter regime where partially polarized states have lowest energy. In the following we have only considered the boundary of stability of the fully polarized ferromagnetic phase.

Figure 1 shows the phase diagram in the $\overline{U}$-J_0 plane for a four-site system with two electrons per band. For this quarter-filled system an orbital superlattice exists, as discussed previously.[6–9] Our results for $J=0$ resemble the results of Gill and Scalapino[9] (GS) obtained for the case $U=\overline{U}+J_0$: ferromagnetism exists for large $\overline{U}$ in a range of values of the intra-atomic exchange J_0. Note, however, that the values of J_0 needed to yield ferromagnetism are much larger than expected to be realistic. The lower dashed line in Fig. 1 is an approximate phase boundary which results from the competition between ferromagnetic and antiferromagnetic exchange, given by[10,9]

$$J_0=\frac{\sqrt{3}-1}{2}\overline{U}. \tag{8a}$$

The upper dashed line is the line

$$J_0=\overline{U}-4t, \tag{8b}$$

where the orbital superlattice becomes unstable as discussed by GS;[9] above that line the nonmagnetic state becomes lower in energy in this case.

When a small interatomic bond-charge repulsion exists, $J=0.25$, the region of ferromagnetism is substantially enlarged, and in particular ferromagnetism exists in the absence of intra-atomic exchange. Furthermore, Fig. 1 shows that only in a narrow range of $\overline{U}$ does the intra-atomic exchange give rise to ferromagnetism when J is present: for example, for $J=0.25$ an increasing J_0 will give rise to ferromagnetism only for $\overline{U}$ in the range 8 to 12. For smaller $\overline{U}$ no ferromagnetism exists for arbitrarily large J_0, and for larger $\overline{U}$ ferromagnetism exists even if $J_0=0$.

The situation is somewhat different for the quarter-filled six-site system, shown in Fig. 2. Here, even in the absence of J ferromagnetism exists even for rather low values of $\overline{U}$ and J_0, and the boundary is close to the approximate boundary Eq. (6a). However, ferromagnetism is not destroyed here as J_0 increases beyond the value given by Eq. (6b). That is, even when the orbital superlattice is destroyed the ferromagnetic itinerant state is lower in energy than the nonmagnetic state. The difference between these results and those for $N=4$ indicates the importance of finite-size effects, and is likely to be due to the fact that the singlet state is nondegenerate for $N=4$ but not for $N=6$. Note that for realistic values of $\overline{U}$ (10 or larger) the required J_0 in the absence of J is larger than would be expected in real materials. In the presence of a small J, the ferromagnetic region is enlarged and substantially smaller values of J_0 are required; in this case, however, a finite value of J_0 is required for ferromagnetism for any $\overline{U}$.

Figure 3 shows a case with the band more than one quarter full, three electrons per band for four sites. In the absence of interatomic J, the values of J_0 required for ferromagnetism are close to the upper limit of what may be considered realistic. Again a small J increases substantially the region in the $\overline{U}$-J_0 plane where ferromagnetism exists.

The tendency to ferromagnetism in this model becomes less pronounced as the band filling decreases. For less than a quarter-filled band we find that no ferromagnetism exists even for infinitely large J_0 when periodic boundary conditions are used. The phase diagram for a $\frac{1}{6}$-filled band (two electrons per band in six sites) is shown in Fig. 4(a). No

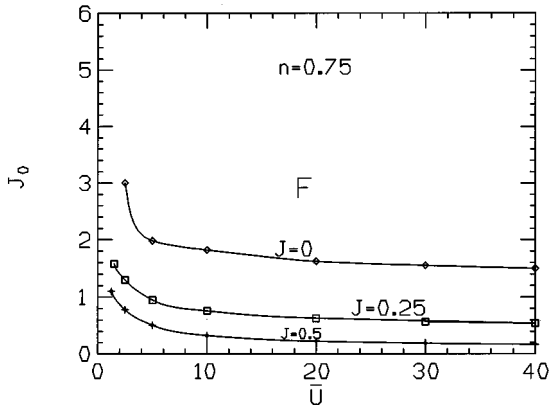

FIG. 3. Same as Fig. 1 for a four-site system with three electrons per band.

ferromagnetism exists for $J=0$, and as J increases the region of ferromagnetism is enlarged. It can be seen that here the intra-atomic exchange suppresses ferromagnetism, never enhances it. In contrast, the interband Coulomb repulsion $\overline{U}$ is necessary for the existence of ferromagnetism if J is small. Figure 4(b) shows the dependence of the phase boundary on lattice size for one value of J for two electrons in N sites, with $N=6$, 8, and 12. It can be seen that the dependence on lattice size is small. Similar results are found for other values of J.

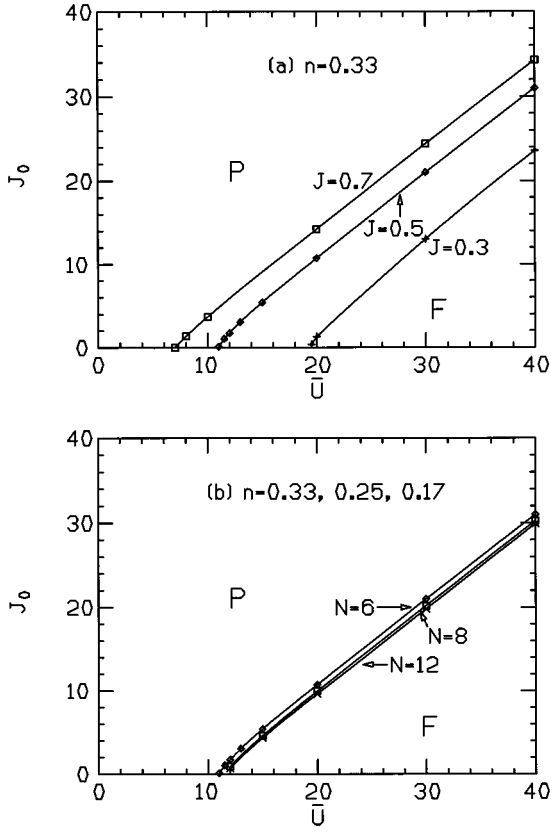

FIG. 4. Phase boundary in the $\overline{U}$-J_0 plane for low band fillings. (a) Two electrons per band in six sites for various values of J. For $J=0$ no ferromagnetism exists. (b) Two electrons per band in lattices of size $N=6$, $N=8$, and $N=12$, for $J=0.5$

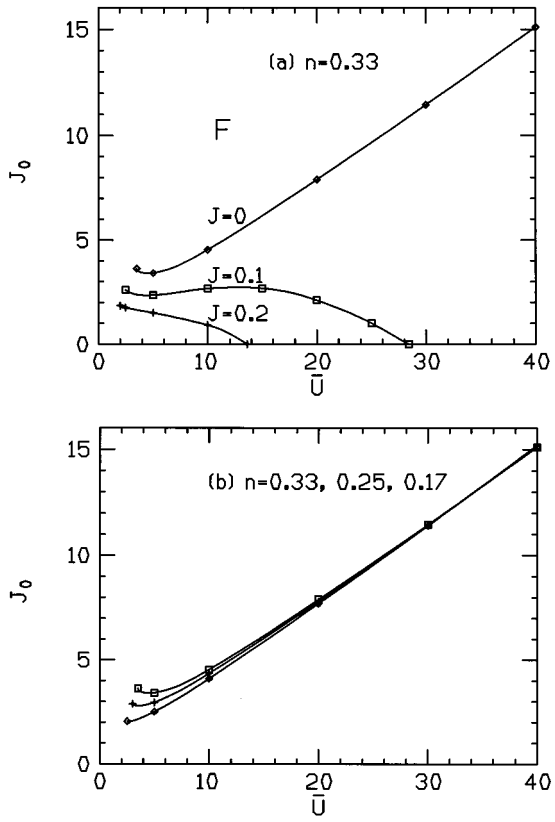

FIG. 5. Phase boundary in the $\overline{U}$-J_0 plane for low band fillings with free ends boundary conditions. (a) Two electrons per band in six sites for various values of J. (b) Two electrons per band in lattices of size $N=6$, $N=8$, and $N=12$, for $J=0$. Increasing N corresponds to decreasing J_0.

If we use free ends boundary conditions instead, however, we find that ferromagnetism can be induced for low electron concentration with J_0 only. Figure 5(a) shows the case of two electrons in six sites, and Fig. 5(b) shows the dependence of the phase boundary on lattice size for $J=0$. For $J=0$ ferromagnetism does occur, although for rather large values of J_0. A small J increases the ferromagnetic region substantially. The reason that ferromagnetism becomes easier for free ends boundary conditions compared to the periodic boundary condition case is that the gain in kinetic energy of the singlet state is reduced. The size of the Hilbert space is larger for the singlet than the triplet sector, but free ends boundary conditions limit the ability of the Hamiltonian to conect these states: for example, for $U\rightarrow\infty$ and/or $\overline{U}\rightarrow\infty$, parts of the Hilbert space become disconnected. For more than one dimension, however, there are more ways for electrons to go around each other independent of the boundary conditions, so that the situation should be more similar to the periodic boundary condition case.

In fact, these results were all obtained for the case of two electrons per band, and as such they may be more representative of that situation than of that for the corresponding band filling (obtained by dividing the number of electrons by the number of sites). For a more reliable indication that these results are representative of the thermodynamic limit, it would be of interest to study the same band fillings for larger

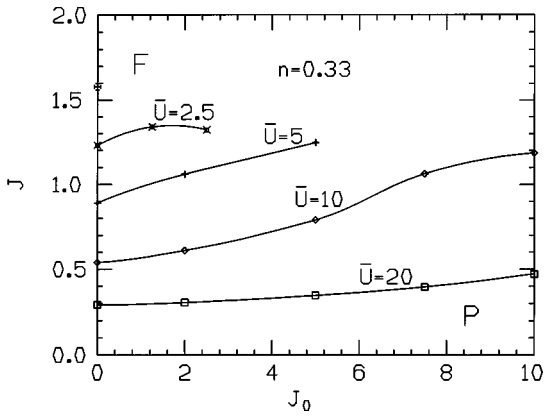

FIG. 6. Phase boundaries in the J-J_0 plane for two electrons per band in six sites and various values of $\overline{U}$ (the boundaries are indicated for $J_0 \leqslant \overline{U}$ only). Above each boundary the system is ferromagnetic.

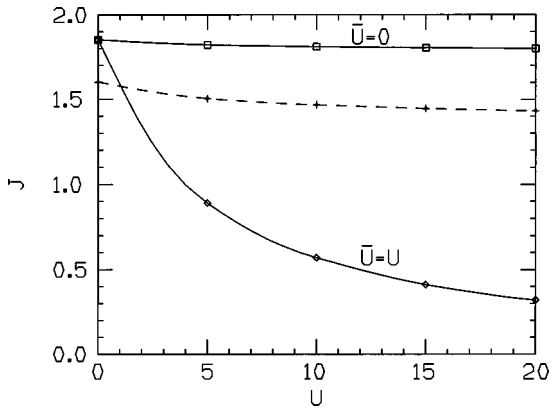

FIG. 8. Phase boundaries in the J-U plane for two electros per band in twelve sites and $\overline{U}=0$ and $\overline{U}=U$. The phase boundary for one band with four electrons in it is also shown (dashed line).

number of electrons. Unfortunately, even to study $n=0.33$ with four electrons on 12 sites involves a Hilbert space of over 3×10^7 states, which is beyond our present capabilities.

We now consider the phase diagrams in the J-J_0 plane for a fixed value of the interband repulsion $\overline{U}$ (and $U=\overline{U}+2J_0$). Figure 6 shows the case of six sites, two electrons per band, for various values of $\overline{U}$. It can be seen that intra-atomic exchange has no favorable effect on ferromagnetism; instead the value of J required for ferromagnetism increases somewhat as J_0 increases. However, the interband Coulomb repulsion strongly favors ferromagnetism, as the required J decreases rapidly with increasing $\overline{U}$.

The fact that J_0 does not help the tendency to ferromagnetism for low band filling is also found for other lattice sizes; Fig. 7 shows the phase boundaries in the J-J_0 plane for two electrons and various lattice sizes for fixed $\overline{U}$ ($\overline{U}=10$). Similarly the fact that $\overline{U}$ favors ferromagnetism is found for other lattice sizes.

As seen from the results in Fig. 6, the interband Coulomb repulsion $\overline{U}$ favors ferromagnetism for low band filling. To examine this further we show in Fig. 8 the boundaries for ferromagnetism for two electrons per band in a 12-site system for $J_0=0$, for the cases $\overline{U}=0$ and $\overline{U}=U$. For the single-band case, the on-site repulsion U in the presence of J strongly favors ferromagnetism for bands close to half full, but the effect of U becomes much less important far away from the half-filled band.[22] In fact, as seen in Fig. 8 for the case of $\overline{U}=0$, which is equivalent to the single-band case, the phase boundary shows only a weak dependence on U for this low band filling. Instead, for $\overline{U}=U$ a rather strong dependence of the phase boundary on the on-site Coulomb repulsion is found, and the J required for ferromagnetism approaches zero as $\overline{U}=U$ tends to infinity. This surprising effect is also found for other lattice sizes and is tied to the fact that there is more than one band in the system. Figure 8 also shows the boundary for four electrons in 12 sites for a single band; while the J required is somewhat lower than for two electrons, the dependence on U is still weak because the system is far from half-filling, in contrast to what happens in the two-band model.

Next we consider the phase diagram in the J-J_0 plane for a reasonable value of the interband Coulomb repulsion, $\overline{U}=10$, The intraband on-site repulsion is taken to be $U=\overline{U}+2J_0$ to obey rotational invariance. Figure 9(a) shows the case of six sites, four electrons per band. Similarly as for two electrons per band, a finite value of the intraband J is required to give rise to ferromagnetism. In contrast, for five electrons in six sites [Fig. 9(b)] the critical J goes to zero as J_0 increases beyond $J_0\sim3$. Qualitatively similar results to the latter are seen for four sites and three electrons per band (Fig. 10), and for eight sites, three electrons and seven electrons per band (Fig. 11).

Finally we consider a case where the ''double exchange'' mechanism operates: a six-site system with six electrons in one band and one electron in the other band. Figure 12 shows the phase diagram in the U-J_0 plane: J_0 by itself will induce ferromagnetism, as expected, especially for large values of the Coulomb repulsion U that will prevent double occupancy of sites for the lower band. However, note that unphysically large values of J_0 are required in the absence of interatomic exchange J. In the presence of a small J, the

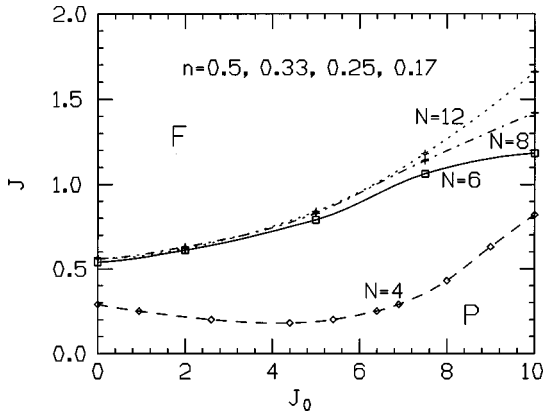

FIG. 7. Phase boundaries in the J-J_0 plane for two electrons per band in lattices of size $N=4$, $N=6$, $N=8$, and $N=12$, for $\overline{U}=10$.

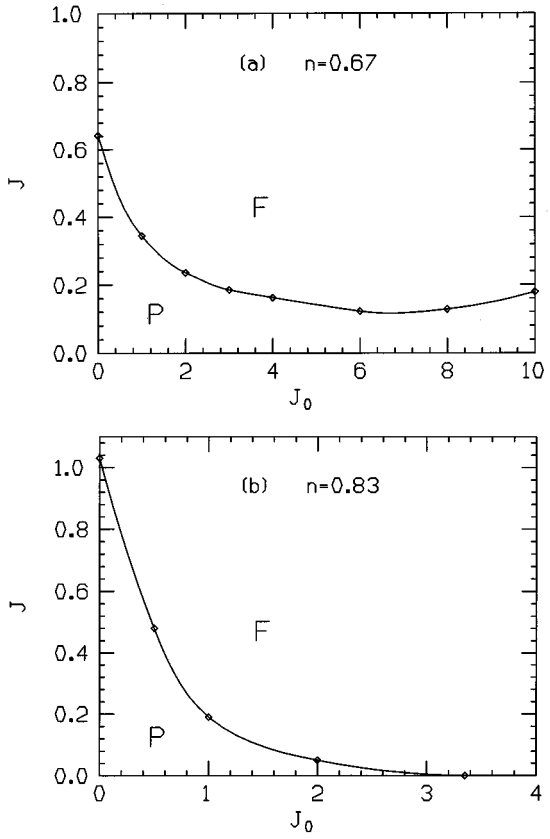

FIG. 9. Phase boundary in the J-J_0 plane for six sites and (a) four electrons per band and (b) five electrons per band. $\overline{U}=10$.

region of ferromagnetism is substantially enlarged and the magnitude of intra-atomic exchange required becomes realistic.

IV. SUMMARY AND CONCLUSIONS

We have studied the combined effect of interband and intraband Coulomb and exchange interactions in a two-band tight-binding model. For a single band, the nearest-neighbor exchange interaction is known to strongly favor ferromagnetism, especially close to half-filling and in the presence of strong on-site repulsion.[20–22,25] For the two-band model, the quarter-filled band case had been thoroughly studied in the past with intra-atomic interactions only.[6–11] For that case, orbital ordering exists for strong Coulomb repulsion, and strong intra-atomic exchange had been found to favor the spin-polarized over the unpolarized case.

However, the orbitally ordered state is insulating for strong interactions. For interactions sufficiently weak that the system is not orbitally ordered, it is also not ferromagnetic. Here we are interested in the description of metallic ferro-

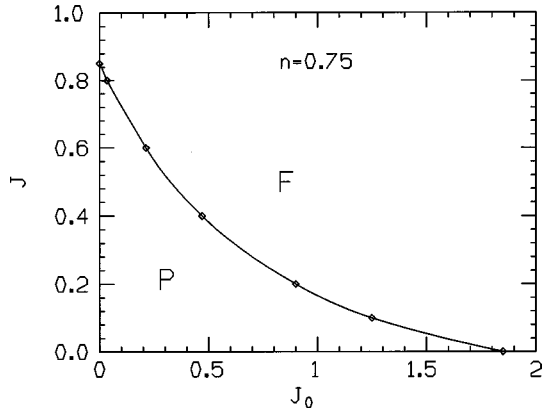

FIG. 10. Phase boundary in the J-J_0 plane for four sites and three electrons per band for $\overline{U}=10$.

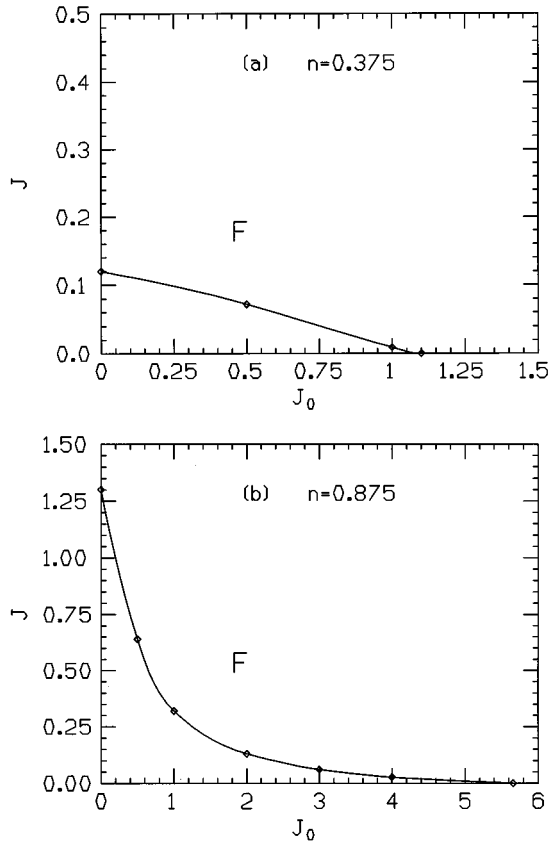

FIG. 11. Phase boundaries in the J-J_0 plane for eight sites and (a) three electrons and (b) seven electrons per band. $\overline{U}=10$.

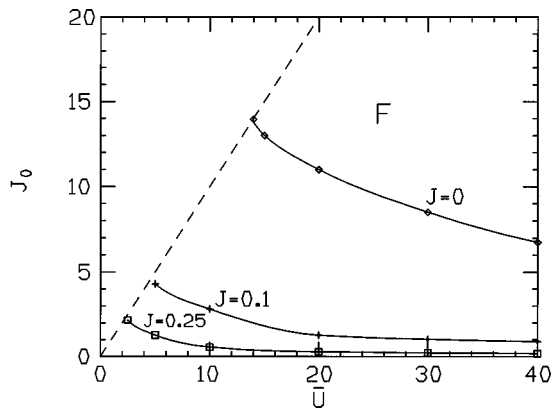

FIG. 12. Phase boundaries in the $\overline{U}$-J_0 plane for six sites and six electrons in one band, one electron in the other band. $U=\overline{U}+2J_0$. The values of J are indicated next to each curve. The dashed line is $J_0=\overline{U}$.

magnetism, and hence we have focused mainly on non-quarter-filled band cases.

The results obtained depend strongly on lattice sizes and band filling, and hence it is not straightforward to extrapolate to the thermodynamic limit. Nevertheless, we believe it is reasonable to expect that results for small systems with a few electrons can give us some qualitative insight into the effect of the various interaction parameters. It is clear that the intra-atomic exchange by itself is often not sufficient to give rise to ferromagnetism, whether for realistic parameters or even for unrealistically large interactions [e.g., Figs. 1, 4, 6, 7, 9, and 11(b)]. Only in some cases did a small J_0 by itself give rise to ferromagnetism [e.g., Figs. 2, 3, 10, and 11(a)]. However, it is likely that the tendency to ferromagnetism in the small systems of this latter group, all of which have an odd number of electrons per band and hence degenerate ground states in the noninteracting case, is substantially larger than it would be in the thermodynamic limit (similar to the case of the Jahn-Teller instability in small molecules which goes over to the weaker Peierls instability for an infinite system). In other cases, both for band fillings smaller and larger than one quarter, no ferromagnetism was found with only J_0. In contrast the interatomic exchange interactions were always found to strongly favor ferromagnetism, even for rather small values of J. Sometimes an added intra-atomic J_0 was found to enhance the tendency to ferromagnetism and other times to suppress it, while the intra-atomic Coulomb repulsion between different orbitals $\overline{U}$ was found to always enhance the tendency to ferromagnetism.

In particular, our results showed that for low band filling, and in particular for the case of two carriers per band, the intra-atomic exchange interaction J_0 is not effective in giving rise to ferromagnetism. This is contrary to the conclusions in the study by Slater, Statz, and Koster[13] which considered a single carrier per band. However, that was a very special nongeneric case, as the cost in kinetic energy in the band caused by spin polarization does not even arise. Instead we believe that the case considered here of two electrons per band, which does take that cost into account, is more likely to be generic for low band fillings. Even though J_0 favors electrons on the same site in different orbitals to have parallel spins, this does not necessarily translate into a tendency for electrons in nearby sites to become spin aligned. Thus we believe that to infer conclusions about the importance of intra-atomic exchange in the tendency to ferromagnetism by estimating the amount of polar fluctuations in d bands[27] is somewhat misleading. Even if there are substantial polar fluctuations (which in our model corresponds to taking a small value of $\overline{U}$) which will give rise to a lowering of energy of two electrons with aligned spin on the same atom, this does not imply that ferromagnetism will result.

We believe that this finding is relevant to the understanding of ferromagnetism in Ni as well as Ni-Cu and Ni-Zn alloy. The magnetic moment of Ni is only about 0.6 Bohr magnetons per atom. Roughly, this is close to full polarization for the case $n=0.33$ obtained for the six-site system with two carriers per band, giving rise to a magnetic moment per atom of $m=0.66\mu_B$ when fully polarized. Note that the carriers in this case are holes rather than electrons. Similarly, the progressively lower band fillings obtained with two carriers per band for increasing lattice sizes could represent alloys of Ni-Cu and Ni-Zn with decreasing Ni concentration and hence decreasing number of d holes per site. Note that it has never been convincingly shown (i.e., beyond mean-field theory) that in a model with only intra-atomic exchange and low density of carriers the ferromagnetic state is the ground state (except for the special case of a single electron per band[13]). The results here show that this is not the case, at least for the case of periodic boundary conditions. Our findings cast doubt on the commonly accepted view that intra-atomic exchange is the driving force for metallic ferromagnetism, at least for nickel and nickel alloys with decreasing d-hole concentration. It is furthermore unlikely that the fundamental mechanism of ferromagnetism would change radically as we move to the left of Ni in the periodic table, as no sharp changes in behavior are seen in alloys with continuously increasing d-hole concentration (e.g., Ni-Fe, etc).

In contrast, we have seen that when intraband interatomic exchange is included, ferromagnetism will result in all cases studied. In some cases, interatomic and intra-atomic exchange were found to act cooperatively. That is, the magnitude of J required to obtain ferromagnetism decreases as the intra-atomic exchange J_0 increases. However, in other cases, particularly for low band filling, J_0 was found to have only a small effect and actually disfavor the tendency to ferromagnetism. That is, a larger value of J is required for larger J_0 to give rise to ferromagnetism. This indicates that the tendency for electrons on the same atom to align their spins parallel to each other is not necessarily relevant to the question whether electrons on different sites in the same band will align their spins parallel to each other. This is, however, strongly dependent on the filling of the bands. For example, for a few carriers in one of the bands and the other band half full, intra-atomic exchange does give a definite tendency for spin alignment through the ''double-exchange'' mechanism. This is well known from analytic work[28] and we have also found it in the numerical calculations discussed here.

In summary, we believe the results of this paper support the view that intraband rather than interband interactions, and interatomic rather than intraatomic interactions, are chiefly responsible for metallic ferromagnetism. Among intraband interactions it is the bond-charge repulsion, which in a tight-binding basis is represented by off-diagonal Coulomb matrix elements giving rise to nearest-neighbor exchange and pair-hopping processes, the one that is likely to be the driving force for metallic ferromagnetism.[20] This view of course does not imply that band degeneracy does not play any role, and in particular we have seen that the intraatomic interorbital Coulomb repulsion $\overline{U}$ plays an important quantitative role even for low density of carriers in favoring ferromagnetism. It also does not exclude the fact that as we move from the left towards the center of the transition-metal series and the magnetization per atom increases, intra-atomic exchange will become quantitatively important. However, it does suggest that the main qualitative features of metallic ferromagnetism can be understood from a simple single-band model, and leaves open the interesting possibility that itinerant ferromagnetism may exist in metals that have not yet been synthesized in the laboratory where intra-atomic exchange can play no role whatsoever, such as hydrogen at very high densities.[26]

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