Broken-symmetry states in solids with multiple bands

P. Thalmeier and L. M. Falicov
Department of Physics, University of California, Berkeley, California 94720
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Calculations are presented which show that an interacting d-electron system can exhibit more general ground states than predicted by a simple Stoner theory of ferromagnetism, which usually neglects effects of d-band degeneracy. The existence of five d subbands leads to a situation where the interaction first changes the population of subbands without destroying spin degeneracy, and thus produces a less metallic but still paramagnetic state. Ferromagnetism occurs for larger values of the interaction. Numerically the calculations are performed for the canonical d bands of face-centered- and body-centered-cubic structures.

I. INTRODUCTION

Transition metals are difficult to understand because of their strongly correlated, narrow d bands. A particularly intriguing example is manganese[1] which occurs in several crystal structures. It has very small electronic transport coefficients compared to its neighbors in the periodic system, chromium and iron. At room temperature, for example $\sigma(\mathrm{Mn})/\sigma(\mathrm{Cr}) = 0.09$ and $\sigma(\mathrm{Mn})/\sigma(\mathrm{Fe}) = 0.07$. This suggests that only a small number of electrons, possibly only s electrons, contribute in the conduction process. The role of the d electrons has not been clearly established. On the one hand as early as 1935 Mott has suggested[2,3] that the d-band states act as traps into which the s electrons may be scattered and lost from the electrical current. In this case a high density of d states results in a low conductivity.

Mott's theory completely neglects the contribution of the d electrons themselves to the conductivity, i.e., it assumes that for all practical purposes the d electrons are localized. However, this hypothesis requires a justification of its own in terms of electron correlations, e.g., the existence of Hubbard-like effects.[4] In fact, it has been proposed[5] that the d band in Mn shows a Hubbard splitting due to d-electron interaction. In principle this could lead to small conductivities if the number of holes in the lower part of the split band is small. However, this kind of "Hubbard splitting" requires a ratio $U/W > 1$, where U and W are the interaction strength of d electrons and their bandwidths, respectively. But it seems that $U/W \simeq 0.6$ is a more representative value for the $3d$-transition series. We show that one can obtain a reduction of the d-electron density of states at the Fermi level and hence a reduction of conductivities in a more natural way, already for values of U/W which are much smaller than 1. The important point is to develop a model which includes the fivefold degeneracy of d states explicitly and study the effect of an intra-atomic d-electron interaction on the occupation of the five orbital d subbands.

It is an established fact that this interaction between the electrons of narrow, partly filled d band can lead to a ferromagnetic ground state, as is the case at the end of the $3d$-transition series. The simplest theory accounting for this phenomenon is the Stoner (Hartree-Fock) theory of itinerant ferromagnetism. In its traditional form however it neglects the effect of orbital d-band degeneracy by replacing it with an s-like single band. In this case one can show that if the interaction strength exceeds a certain limit, which is given by the Stoner criterion, the electronic system can lower its total energy by removing the spin degeneracy of band occupation, thus lowering the Coulomb correlation energy at the expense of the one-electron band energy. Such a simple behavior however, is due to the total neglect of orbital degeneracy in the d band. If we explicitly include the existence of five orbital subbands (i.e., ten spinbands), the Coulomb correlation energy of d electrons directly depends on the occupation of each of the ten spinbands. (See Ref. 6, denoted as I in the rest of this paper). This means, however, that the d electrons can change their total energy by rearranging the occupation of ten spinbands (subject to one constraint) instead of the occupation of only two spinbands as in the simple Stoner model.

Full d-band calculations have been carried out for ferromagnetic transition metals by including spin-polarized effects.[7–12] This is accomplished either by means of a spin-dependent local-density approach or by the use of the unrestricted Hartree-Fock approximation. In addition more sophisticated Stoner-like criteria for ferromagnetism have been developed for d-like materials, again within the context of local-density theory.[13–15] However, systematic calculations based on band occupation and on the relative strengths of d-band width and intra-atomic (local) repulsion have not included the multiple bands in detail.[16] Specifically one could suggest that because of the existence of five spinband pairs the d electrons

might find a state of lowest energy by changing the occupation of spinbands in pairs, without breaking spin degeneracy and hence avoid ferromagnetic order. Such a rearrangement should have a pronounced effect on the density of states at the Fermi level and thus change primarily the conductive properties instead of the magnetic ones. Therefore we should expect that the orbital degeneracy in d bands, and hence the greater variety of possible spinband occupations, might allow for more types of ground states than the simple Stoner model would predict.

To show that these ideas are correct, we have performed calculations with a model system already used in I. We take again the canonical d bands of Andersen[17–19] as a starting point and assume that the Coulomb interaction between the d electrons is of purely intra-atomic nature. Hybridization with s bands is neglected in all our discussions, its main effect is accounted for by allowing a nonintegral occupation of the d bands. These basic ingredients of our calculations, which are performed for bcc and fcc structures, are described in Sec. II. To develop a feeling for the effects of degeneracy, Sec. III describes a modified Stoner model which already explicitly includes the ten spinbands but still is restricted to ground states which only account for the possible removal of spin degeneracy as in the simple Stoner model. Section IV is the main part of the present paper and explicitly discusses the ideas outlined above. Section V finally gives the conclusions.

II. CANONICAL BANDS, BAND ENERGY, AND CORRELATION ENERGY

As a starting point for our calculations we assume that the d-electron states are well described by Andersen's canonical bands[17–19] which are equivalent to one-parameter tight-binding bands (see I for more details). The canonical d band consists of five spinband pairs (1,2), (3,4), . . . , (9.10) which are ordered according to their energies, i.e.,

$$E_{1,2}(\vec{k}) \leqslant E_{3,4}(\vec{k}) \leqslant \cdots \leqslant E_{9,10}(\vec{k})$$

for every k vector of the Brillouin zone. All we need for our calculations are $D_\nu(E)$ the partial densities of states (PDOS), and $n_\nu(E)$ the partial number of occupied states (PNOS) for each of the spinbands $E_\nu(k)$ where $\nu = 1, 2, \ldots, 10$. These functions are shown in I.

A. Band energy

From the PDOS one can calculate the band energy in the one particle, noninteracting ground state of the d electrons (E_F^0 is the Fermi level, W the bandwidth)

$$E_b(E_F^0) = \sum_\nu E_b^\nu(E_F^0) \ ,$$
$$E_b^\nu(E_F^0) = \int_{-\infty}^{E_F^0} D_\nu(E) E \, dE \ . \tag{2.1}$$

The center of gravity of the complete d band has been set to 0. The E_b^ν functions give the band energy of each spinband ν. This is shown in Fig. 1 for the bcc and fcc structures. One can see that the five twofold-degenerate E_b^ν functions are separated in two groups. The lower group corresponds to the e_{2g}-type subbands, the upper group to the t_{2g}-type bands.[6] The sum of these individual subband energies gives

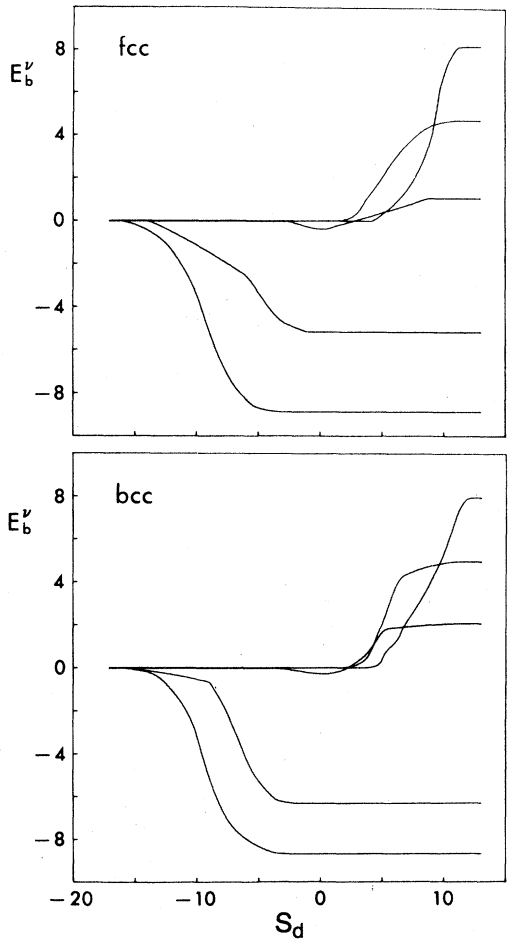

FIG. 1. Lower diagram: integrated subband energies for the bcc canonical bands, where $\nu = (1, 2), \ldots, (9, 10)$ is the spinband index. The order is according to increasing energy for totally filled bands. Upper diagram: the same for the fcc canonical bands. The abscissas are the structure constant S_d which are related to the Fermi energy by the linear transformation $E_F^0 = S_d(W/28.5)$ for bcc and $E_F^0 = S_d(W/27.6)$ for fcc. Similarly the ordinates are in units of $(W/28.5)$ for bcc, and $(W/27.6)$ for fcc.

the total band energy, as already shown in Ref. 19. It has a parabolic shape as a function of Fermi energy E_F^0 and vanishes for empty and filled d bands. The subband kinetic energies E_b^ν converge to constants for completely filled bands. They correspond to the center-of-gravity energy of each subband. The sum of these energies is zero because of our choice of the center of gravity of the whole band.

B. Intra-atomic correlation energy

In order to perform the investigations outlined in the Introduction we have to choose a specific model for the interaction between d electrons. As in I, we assume that it is well described by the multiband Hubbard interaction[20]

$$V_c = \frac{1}{2} U \sum_{i\nu\nu'} a_{\nu i}^\dagger a_{\nu' i}^\dagger a_{\nu' i} a_{\nu i} \quad . \tag{2.2}$$

Here $a_{\nu i}^\dagger$, $a_{\nu i}$ denote the creation and destruction operators for the ten ($\nu = 1, \ldots, 10$) Wannier orbitals at a given site i. They are connected to the Bloch operators of band states $c_{\nu\vec{k}}$, $c_{\nu\vec{k}}^\dagger$ via the transformation

$$a_{\nu i} = (N)^{-1/2} \sum_{\vec{k}} \exp(-i\vec{k}\cdot\vec{R}_i) c_{\nu\vec{k}} \quad , \tag{2.3}$$

and its Hermitian conjugate. In Eq. (2.2) several approximations have been made: (i) only on-site interactions of d electrons are included; (ii) exchange interactions between different orbitals have been neglected by assuming that they are small with respect to the direct Coulomb interaction; (iii) the direct Coulomb interaction between different Wannier orbitals is assumed to be a constant U, independent of the type of orbital involved.

The first-order perturbative correction to the band energy is given by the expectation value of V_c with respect to the noninteracting ground state, which consists of canonical band states filled to the Fermi level E_F^0. Up to a constant this energy has previously been called the "intra-atomic correlation energy." We maintain this nomenclature here. We have shown that this energy is given by

$$E_c(E_F^0) = \frac{1}{2} U \sum_\nu n_\nu(E_F^0)[1 - n_\nu(E_F^0)] \quad , \tag{2.4}$$

$$n_\nu(E_F^0) = \int_{-\infty}^{E_F^0} D_\nu(E)\, dE, \quad 0 \le n_\nu \le 1 \quad ,$$

$$n(E_F^0) = \sum_\nu n_\nu(E_F^0), \quad 0 \le n \le 10 \quad .$$

Therefore the knowledge of the PNOS functions which describe the occupation of each subband is sufficient to calculate the correlation energy. Because the total number of states $n(E_F^0)$ is a monotonic function of E_F^0, the band and correlation energies can also be expressed as a function of n. The behavior of $E_c(n)$ was discussed in I.

C. Total energy, relative stability of bcc and fcc structures

The total energy of the interacting d electrons is given by

$$E_T(n) = E_b(n) + E_c(n) \quad . \tag{2.5}$$

It determines in which region of the (U,n) plane the bcc or fcc structure is stable, according to whether $E_T(\text{bcc}) \lesseqgtr E_T(\text{fcc})$. As an illustration this is shown in Fig. 2. The base line $U = 0$ shows which stability regions the band energy alone would predict. This agrees with Andersen and Jepsen's result.[19] For increasing U, the stability region for the bcc phase decreases somewhat, especially in the middle region around $n \simeq 4$. For U/W larger than ~ 0.4 two new stability regions for the bcc phase occur, one of them ($n \simeq 8$), however, is very narrow and the difference there is very small. The results are interesting insofar as inclusion of the correlation energy does not change the picture very dramatically as compared to the consideration of the band energy alone. One cannot expect, however, that such a simple calculation gives a correct picture for the whole $3d$-transition-metal series because the energy differences of bcc and fcc structures are only a few percent or less of the total-band and correlation energies. In fact Fig. 2 predicts a stable bcc phase for large n, whereas in reality the fcc phase is observed at the end of the transition-metal series.

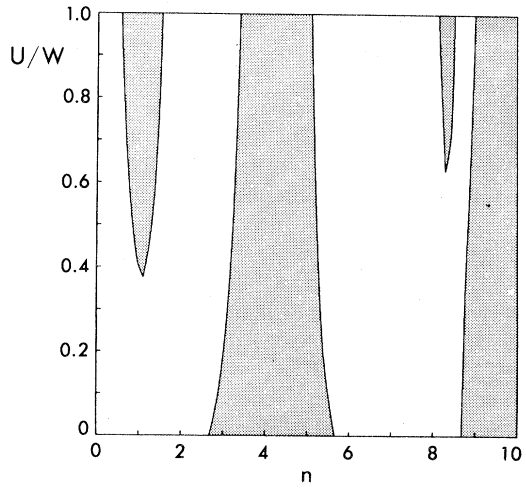

FIG. 2. Stable regions for bcc (shaded) and fcc (white) structures; W is the average bandwidth defined by $W = \frac{1}{2}(W_{\text{bcc}} + W_{\text{fcc}})$ where we assume the same ratio $(W_{\text{bcc}}/W_{\text{fcc}}) = 28.5/27.6$ as for the canonical bandwidths.

III. SPIN-POLARIZED CALCULATIONS, STONER MODEL FOR MULTIPLE BANDS

A. Review of the one-band Stoner model

In the case of a single band the possibility of magnetic ordering due to electronic correlation has been extensively discussed. For several reviews, see Ref. 21. The conventional Stoner model starts with the assumption that effects due to the existence of five orbital d subbands can be neglected and introduces an interaction (Hubbard interaction)

$$V_c^s = U \sum_i a_{\uparrow i}^\dagger a_{\uparrow i} a_{\downarrow i}^\dagger a_{\downarrow i} \ , \tag{3.1}$$

where $a_{\sigma i}^\dagger$ (σ is the spin index) is assumed to create any d state, irrespective of which subband it belongs to. With Eq. (3.1) the total energy of the system is given by

$$E_T(n_\uparrow, n_\downarrow) = E_b(n_\uparrow, n_\downarrow) + U n_\uparrow n \ , \tag{3.2}$$

where $n_\uparrow$ and $n_\downarrow$ are the partial occupations of the two spinbands, constrained by $n_\uparrow + n_\downarrow = n$. From Eq. (3.2), it is obvious that for large enough U the d electrons prefer a ferromagnetic ground state. The critical condition for onset of magnetic ordering, obtained from calculating the local minimum of $E_T(n_\uparrow, n_\downarrow)$ is expressed by the well-known "Stoner criterion"

$$U_c D(E_F^0) = 1 \ . \tag{3.3}$$

For U larger than the value determined from Eq. (3.3), a magnetic moment develops due to different occupation of spinbands, i.e., $n_\uparrow \neq n_\downarrow$. One can describe this in two ways: In the "quasiparticle picture" the quasiparticle energies $\epsilon_\nu(\vec{k})$ derived from Eq. (3.2) depend on spin direction according to

$$\begin{aligned} \epsilon_\nu(\vec{k}) &= E_\nu(\vec{k}) + U n_\downarrow, \quad \nu \text{ odd} \ , \\ \epsilon_\nu(\vec{k}) &= E_\nu(\vec{k}) + U n_\uparrow, \quad \nu \text{ even} \ . \end{aligned} \tag{3.4}$$

Different occupation of spin-up (odd) and -down (even) bands in this picture is due to shifted quasiparticle densities which arise from occupations of states $\epsilon_\nu(\vec{k}) < E_F$, with a common Fermi level E_F. In view of our objectives, however, we prefer an equivalent but more convenient picture. We stay with the noninteracting, i.e., nonsplit particle spectrum and label the states by the band energies $E_\nu(\vec{k})$. The interaction thus leads to different Fermi levels, $\mu_\uparrow$ for spin-up (odd) bands and $\mu_\downarrow$ for spin-down (even) bands if $U > U_c$. This in turn gives different occupation of spinbands according to

$$n_\sigma = \int_{-\infty}^{\mu_\sigma} D(E)\, dE \ , \quad n_\uparrow + n_\downarrow = n \ . \tag{3.5}$$

Application of this conventional one-band Stoner model to the fivefold degenerate d bands using the interaction V_c^s, however, has a serious drawback. According to Eq. (3.1) the model assumes that any two electrons with parallel spins do not interact. If there is only one orbital state, this is certainly true because of the Pauli principle. However if there are five orbital states it seems much more reasonable to assume that electrons with parallel spins but in different orbitals have about the same interaction strength as those with antiparallel spins. In fact this is the basic approximation in our interaction Hamiltonian Eq. (2.2) which therefore should be a more reasonable starting point for considering the magnetic properties of a fivefold degenerate d band.

B. Stoner model for the degenerate case

To find out which magnetic state characterized by $(n_\uparrow, n_\downarrow)$ is stable for a given (n, U) we consider again the total energy $E_T(n_\uparrow, n_\downarrow)_{n,U}$ and look for the minimum as a function of $n_\uparrow, n_\downarrow$. Now

$$\begin{aligned} E_T(n_\uparrow, n_\downarrow) &= E_b(n_\uparrow, n_\downarrow) + E_c(n_\uparrow, n_\downarrow) \ , \\ E_b(n_\uparrow, n_\downarrow) &= \int_{-\infty}^{\mu_\uparrow} E D(E)\, dE + \int_{-\infty}^{\mu_\downarrow} E D(E)\, dE \ . \end{aligned} \tag{3.6}$$

Again $\mu_\uparrow, \mu_\downarrow$ have to satisfy Eq. (3.5). Furthermore

$$E_c(n_\uparrow, n_\downarrow) = \tfrac{1}{2} U \sum_{l,\sigma} n_l(\mu_\sigma)[1 - n_l(\mu_\sigma)] \ , \tag{3.7}$$

where $l = 1, \ldots, 5$ denotes the orbital subbands and $\sigma = \uparrow, \downarrow$ the spin direction, i.e., $\nu = (l, \sigma)$. To find the minimum of $E_T(n_\uparrow, n_\downarrow)$ we calculate its derivatives with respect to $n_\uparrow, n_\downarrow$ or, equivalently, with respect to $\mu_\uparrow, \mu_\downarrow$. Because of $n_\uparrow + n_\downarrow = n$, the variables are not independent and it is more convenient to calculate $(\partial E_T / \partial \Delta)_n$, where $\Delta = \mu_\uparrow - \mu_\downarrow$ is the "exchange splitting."

By means of the relation

$$\left(\frac{\partial \mu_\downarrow}{\partial \mu_\uparrow} \right)_n = \frac{D(\mu_\uparrow)}{D(\mu_\downarrow)} \ , \tag{3.8}$$

one can easily compute $(\partial E_T / \partial \Delta)_n$, and equating this expression to 0 one obtains the general condition for the existence of a ferromagnetic state:

$$1 = \frac{U}{\Delta} \sum_l d_l(n, \Delta) m_l(n, \Delta) \ , \tag{3.9}$$

where

$$\begin{aligned} d_l(n, \Delta) &= \frac{[D_l(\mu_\uparrow) + D_l(\mu_\downarrow)]}{[D(\mu_\uparrow) + D(\mu_\downarrow)]} \ , \\ m_l(n, \Delta) &= n_l(\mu_\uparrow) - n_l(\mu_\downarrow) \ , \\ m &= \sum_l m_l, \quad D(\mu_\sigma) = \sum_l D_l(\mu_\sigma) \ . \end{aligned}$$

This, together with Eq. (3.5) determines the general ferromagnetic solution. Here we only discuss the limiting cases: (i)

$$m \to 0+ \quad (\text{i.e., } \Delta \to 0+, \quad \mu_\uparrow = \mu_\downarrow = \mu) \ .$$

Because $m_l(n,\Delta)/\Delta \to D_l(\mu)$, Eq. (3.9) simplifies to

$$1 = U \sum_l D_l^2(\mu)/D(\mu) \ . \tag{3.10}$$

This is the equivalent of the Stoner criterion Eq. (3.3) in the single-band case. In fact for one band Eq. (3.10) reduces to Eq. (3.3). Equation (3.10) determines the boundary between the paramagnetic and ferromagnetic phase in the (U,n) plane; (ii)

$$m = \begin{cases} n, & 0 \leq n \leq 5 \ , \\ 10-n, & 5 \leq n \leq 10 \ . \end{cases}$$

In this case either $\mu_\downarrow$ is at the bottom of the first ($l=1$) band and therefore $D(\mu_\downarrow)=0$ for $0 \leq n \leq 5$, or $\mu_\uparrow$ is at the top of the uppermost ($l=5$) band and thus $D(\mu_\uparrow)=0$ for $5 \leq n \leq 10$. In either case Eq. (3.9) reduces to

$$1 = \frac{U}{\Delta} \sum_l \frac{D_l(\mu)}{D(\mu)} n_l(\mu) \ , \tag{3.11}$$

where

$$\mu = \begin{cases} \mu_\uparrow, & 0 \leq n \leq 5 \\ \mu_\downarrow, & 5 \leq n \leq 10 \ , \end{cases}$$

and

$$\Delta = \begin{cases} \mu_\uparrow - E_B, & 0 \leq n \leq 5 \\ E_T - \mu_\downarrow, & 5 \leq n \leq 10 \ . \end{cases}$$

Here E_B, E_T denote the bottom and top of the d band and m is the maximum possible magnetization for a d band with n electrons. Therefore Eq. (3.11) describes the boundary between the region of "strong ferromagnetism," i.e., complete magnetization and the region of partial magnetization where m is smaller than its maximum possible value.

The phase boundaries calculated according to Eqs. (3.10) and (3.11) for canonical d bands in bcc and fcc structures are shown in Fig. 3. As expected the critical values depend strongly on the d-band occupation n. On the average, the transition from the paramagnetic to a ferromagnetic state takes place for values of $U/W \sim 0.25$–0.3. For bcc the narrow region around $n \simeq 4$ in which the d electrons stay paramagnetic for values up to $U/W = 1$ is due to a very small overlap of the e_{2g}- and t_{2g}-type subbands as can be seen in Fig. 1 of I. There are mainly two regions for both bcc and fcc d bands (dark shading in Fig. 3) where strong ferromagnetism, i.e., no minority spins,

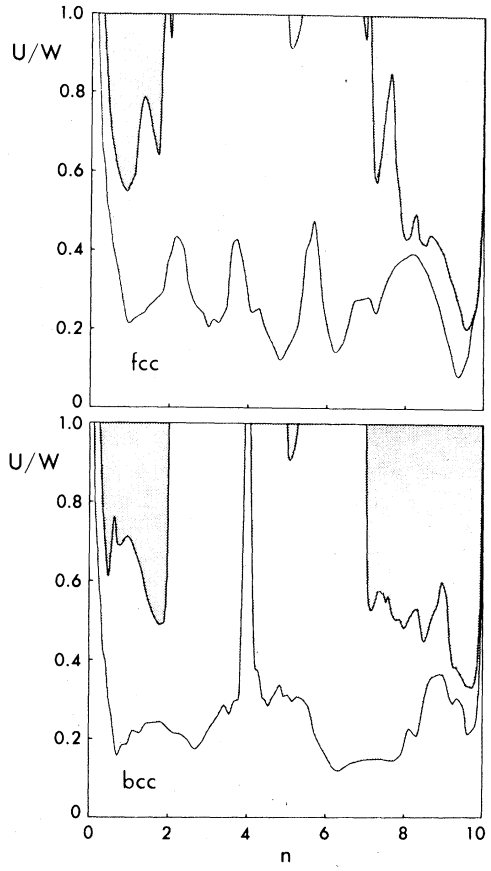

FIG. 3. Lower diagram: stable regions for totally polarized ferromagnetic (dark shading), partially polarized ferromagnetic (light shading), and paramagnetic (white) canonical d bands for bcc structure. Upper diagram: the same for fcc canonical bands.

is predicted. The first region has only a small number of d electrons $n \lesssim 2$, the second one lies at $n \gtrsim 7$. For occupation in between $2 < n < 7$ strong ferromagnetism is clearly disfavored. Qualitatively this is in agreement with the situation in $3d$ transition metals where (strong) ferromagnetism is only observed at the end of the series for Fe($n \simeq 7.1$), Co($n \simeq 8.4$), and Ni($n \simeq 9.4$). However there is no ferromagnetism at the lower end of the series as predicted in this simple theory. This discrepancy can be due to two effects. First, because of extended d-wave functions the ratio U/W for small n must be smaller than at the upper end of the series. Second, for a small number of $3d$ electrons the effect of a $4s$ band cannot properly be neglected. In this case the electronic system can decrease its total energy by filling up the wide and weakly correlated s band instead of splitting up the d band.

IV. GENERAL THEORY OR REARRANGEMENT IN d-BAND OCCUPATIONS DUE TO d-ELECTRON INTERACTION

In the case of noninteracting d electrons the knowledge of the Fermi level E_F^0 or equivalently the d-band occupation n determines the ten spinband occupations $n_{l\sigma}(E_F^0)$ uniquely. We have seen in Sec. III that in the presence of an intra-atomic d-electron interaction a rearrangement of spinband occupations can lead to a lower total energy and therefore to a more stable electronic state. The rearrangement for a Stoner-like ferromagnet happens in such a way that each of the five subband occupations $n_{l\uparrow}(\mu_\uparrow)$, $n_{l\downarrow}(\mu_\downarrow)$ is determined by a single parameter, the Fermi level ($\mu_\uparrow$ or $\mu_\downarrow$, respectively). As already mentioned in the Introduction, this is a very restricted type of rearrangement.

It is the main topic of this paper to show that in a d band with its fivefold orbital degeneracy there exist more general rearrangements of spinband occupations which lead to a lower energy but which do not necessarily produce a Stoner ferromagnetic state. The idea is simply to consider the total energy of the interacting d electrons as a function of nine parmeters, i.e., the ten occupation numbers $n_{l\sigma}(\mu_{l\sigma})$ subject to the constraint.

$$\sum_{l\sigma} n_{l\sigma}(\mu_{l\sigma}) = n \quad , \tag{4.1}$$

where now the different $n_{l\sigma}$ are no longer restricted to having common Fermi levels $\mu_\uparrow$, $\mu_\downarrow$ but rather they are allowed arbitrary values by associating an individual Fermi level $\mu_{l\sigma}$ with every spinband. Then, in the most general case, for a given U/W, we have to look for the minimum of the total energy $E_T(\{n_{l\sigma}\})$ as a function of ten parameters $\{n_{l\sigma}\}$, subject to Eq. (4.1)

$$E_T(\{n_{l\sigma}\}) = \sum_{l\sigma} \int_{-\infty}^{\mu_{l\sigma}} D_l(E) E \, dE + \tfrac{1}{2} U \sum_{l\sigma} n_{l\sigma}(\mu_{l\sigma})[1 - n_{l\sigma}(\mu_{l\sigma})] \quad . \tag{4.2}$$

It is not really necessary to minimize Eq. (4.2) with respect to all occupation numbers but rather one has to vary only those corresponding to spinbands which are partially filled for $U = 0$. This is so because one requires a minimum thereshold (energy gap) to gain in total energy by starting to occupy completely empty spinbands or to empty completely filled spinbands. In Figs. 1 and 2 of I it can be seen that at most six spinbands (three orbital subbands) can be partially filled for a given occupation n in the paramagnetic normal state. Thus, considering Eq. (4.1) we have initially to minimize the total energy with respect to five parameters at most. Before going into discussing numerical calculations we want to bring an intuitive argument why in general, for relatively large (U/W) one should not expect that the lowest-energy state is always the one whose magnetic symmetry is broken, i.e., $n_{l\uparrow} \neq n_{l\downarrow}$. Rather, one can have a situation where pairwise rearrangement, preserving spin degeneracy, can lead to a more stable state. Assume that for a certain n only two orbitals, l and l', are partly filled so that $n_{l\sigma} > 0.5$, $n_{l'\sigma} < 0.5$. Consider first a variation of occupation numbers where spin degeneracy is destroyed, i.e., $\delta n_{l\uparrow}$, $\delta n_{l'\uparrow} > 0$ and $\delta n_{l\downarrow}$, $\delta n_{l'\downarrow} < 0$. Then, according to Eq. (4.2) the band energy increases, correlation energies decrease for the $(l\uparrow)$ and $(l'\downarrow)$ spinbands and increase for $(l\downarrow)$ and $(l'\uparrow)$. Thus the contributions to the variation of E_c tend to compensate. On the other hand, considering a variation $\delta n_{l\sigma} = \delta n_l > 0$, $\delta n_{l'\sigma} = \delta n_{l'} < 0$ which preserves spin degeneracy, we see that the contributions to E_c of all four $(l\sigma)$, $(l'\sigma)$ spinbands decrease; the kinetic energy increases as before. More formally, this can be seen by considering the gradient of Eq. (4.2).

$$\left(\frac{\partial E_T}{\partial n_\nu}\right)_n = \mu_\nu - \mu_{\nu_0} - U(n_\nu - n_{\nu_0}) \quad , \tag{4.3}$$

where $\nu = (l\sigma)$, $(l'\sigma)$, and ν_0 is an arbitrary but fixed spinband which is partly filled.

Altogether under the above conditions the variations which preserve spin degeneracy should lead to a state of lower energy than the first type of variation which produces a magnetic state. In other words, there should be situations where the interacting d-electron system prefers to empty some spinband pairs and fill others rather than splitting them to produce a magnetic moment. This type of rearrangement with pairwise change of subband occupation should have a drastic effect on the density of states at the Fermi level, given by

$$D(E_F) = \sum_{l\sigma} D_l(\mu_{l\sigma}) \quad , \tag{4.4}$$

where E_F denotes the true Fermi level in the quasiparticle picture. Under conditions discussed above one would expect a decrease in $D(E_F)$. Thus, roughly speaking one could say that rather than exhibiting a paramagnetic-ferromagnetic phase transition at a certain critical value of U/W described by Eq. (3.10), the d-electron system prefers first to lower its $D(E_F)$—in other words, to become less metallic—in such a way that it remains paramagnetic but with different subband occupation for a sizable range of U values. At still higher values of U, a transition to a partially ferromagnetic state takes place which involves the polarization of the only spinband pair which is still partially occupied.

Before we discuss the numerical calculations it is necessary to comment on the meaning of our generalized variational procedure in terms of the quasi-

particle picture. In this picture, the variation of occupation numbers $n_{l\sigma}$ corresponds to a rigid shifting of subband energies and subband densities of states according to

$$\epsilon_\nu(\vec{k}) = E_\nu(\vec{k}) + U \sum_{\nu' \neq \nu} n_{\nu'} \quad (\nu = l, \sigma) \ . \quad (4.5)$$

A rigid shifting of subbands neglects the fact that PDOS which are overlapping for $U = 0$ exchange some of their spectral weight when shifted according to Eq. (4.5). This can be easily seen by recalling that in our context subbands are defined according to increasing energy at every $\vec{k}$ point (cf. Sec. II). This means that during shifting, described by Eq. (4.5) the subbands do not stay rigid but rather change their shape in their respective overlapping energy range. However in a first approximation we neglect this effect and assume that the PDOS functions are shifted rigidly. In our picture this means that we look for a minimum of total energy by simply varying occupation numbers $n_{l\sigma}(\mu_{l\sigma})$ without changing their functional dependence on the Fermi levels $\mu_{l\sigma}$.

We now discuss numerical calculations for several typical d-band occupations using the bcc and fcc canonical d bands. The configuration $\{n_{l\sigma}\}$ which minimizes the total energy is found in the following way: we know the solution for $U = 0$ which is given by $n_{l\sigma} = n_{l\sigma}(E_F^0)$, $\mu_{l\sigma} = E_F^0$. We take this as a starting point and follow the course of the minimum numerically as U gradually increases, allowing all $\mu_{l\sigma}(n_{l\sigma})$ for partially filled bands to vary and satisfying the constraint Eq. (4.1). The reliable accuracy of the determined set of $\{n_{l\sigma}\}$ which minimizes the total energy is about two percent. In the following we discuss the behavior of spinband occupation numbers as a function of increasing U.

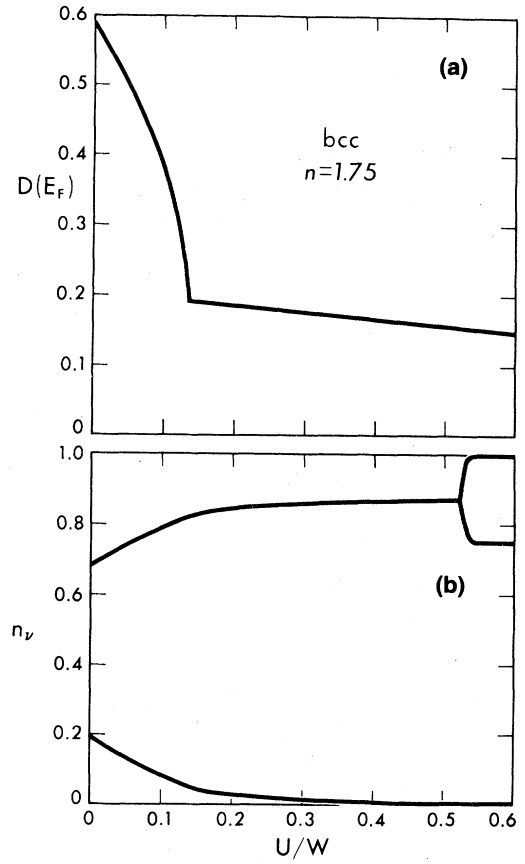

FIG. 4. Body-centered cubic, $n = 1.75$. Lower diagram (b): occupation numbers for the spinbands $\nu = (1, 2)$ (occupation more than 0.5) and $\nu = (3, 4)$ (occupation less than 0.5) as functions of the interaction strength. Upper diagram (a): density of states at the Fermi level. A small kink at $(U/W) = 0.53$, due to the magnetic splitting, has been omitted because it is within numerical accuracy.

A. Body-centered cubic, $n = 1.75$

For this n only the lowest four spinbands (two orbital subbands) are partially occupied, all others are empty. Denoting spinbands again with $\nu = 1, 2, \ldots, 9, 10$ according to increasing energy, the pair (1,2) is more than half filled, (3,4) less than half filled. This corresponds to the situation discussed qualitatively above. There are altogether three variational parameters for the energy minimization. Figure 4 shows that the behavior of spinband occupations for the lowest-energy state confirms our qualitative expectations. For $0 \leq (U/W) \lesssim 0.4$ the (3,4) spinband pair is emptied, whereas (1,2) are filled together at the same time thereby strongly reducing the correlation energy. No splitting of spin-up and -down bands is observed. For $0.4 < (U/W) < 0.5$ the upper bands (3,4) are already completely empty and nothing changes with respect to (1,2) whose occupation numbers are both 0.875. Only if $(U/W) > 0.53$ it is energetically more favorable to destroy spin degeneracy and split (1,2) so that finally $n_1 = 1$, $n_2 = 0.75$ which describes a partially polarized ferromagnetic state which only involves bands 1 and 2. The top part of Fig. 4 shows the behavior of the density of states $D(E_F)$ in the same range of (U/W). We see that as long as the occupations of bands (1,2) and (3,4) are changed in pairs, $D(E_F)$ decreases drastically because the individual Fermi levels μ_ν $(\nu = l\sigma)$ approach the bottom or top of the subbands. Then $D(E_F)$ slowly approaches a constant which is determined by the density of states of the only remaining subband partially filled $(n_2 = 0.75)$.

B. Face-centered cubic, $n = 1.75$

This case, shown in Fig. 5, exhibits the same qualitative features as in Sec. IV A, only the characteristic values of U are somewhat smaller. Again, due to the emptying and filling of spinbands pairs, the density of states $D(E_F)$ decreases with increasing U. The structure in $D(E_F)$ at $(U/W) = 0.4$ is caused by the magnetic transition.

C. Body-centered cubic, $n = 6$

Again, as can be checked by looking at Fig. 1 in I, this is a case where only four spinbands (5,6) and (7,8) are partially filled. The lower e_{2g} pairs (1,2) and (3,4) are already full and therefore of no concern. Figure 6 shows the behavior of $n_{(5,6)}$ and $n_{(7,8)}$ as functions of U. No magnetic splitting develops. Instead, already at $(U/W) = 0.15$, the pair (5,6) is full and (7,8) empty. Correspondingly $D(E_F)$ shows

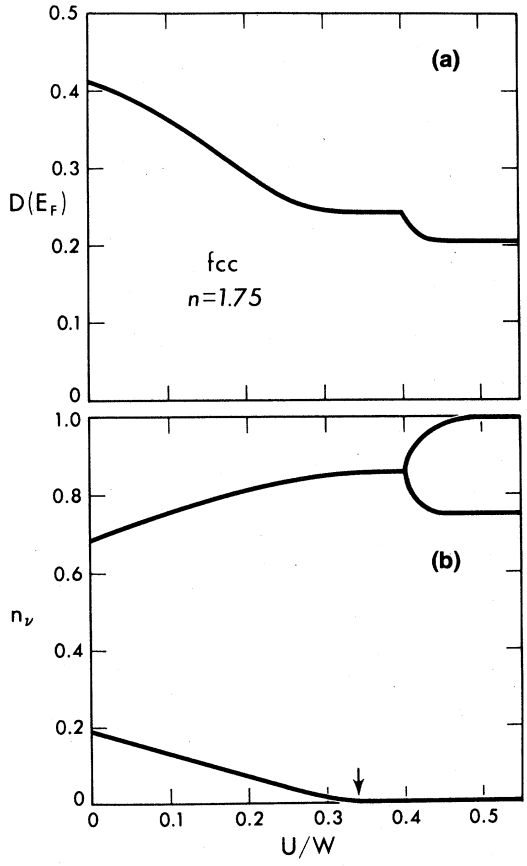

FIG. 5. Face-centered cubic, $n = 1.75$. Lower part (b): occupation numbers for spinbands $\nu = (1, 2)$ (upper curves) and $\nu = (3, 4)$ (lower curve). Upper part (a): corresponding density of states at the Fermi level.

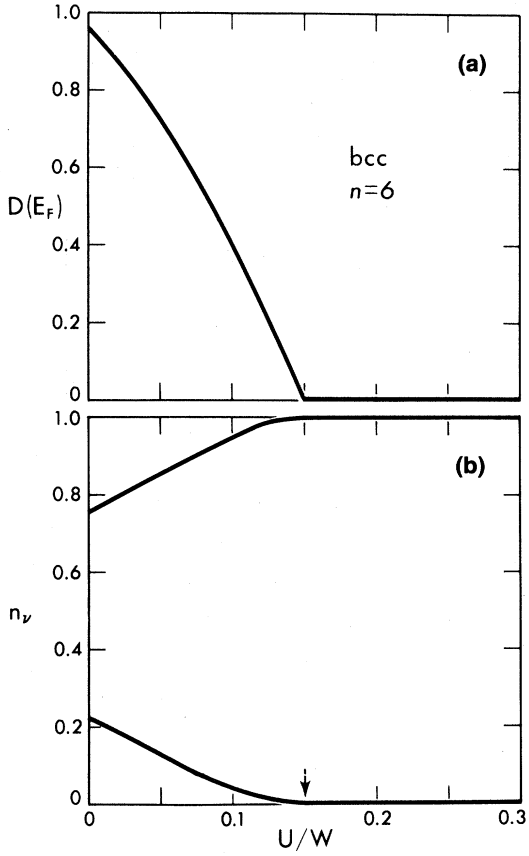

FIG. 6. Body-centered cubic, $n = 6$. Lower part (b): occupation numbers for spinbands $\nu = (5, 6)$ (upper curve) and (7,8) (lower curve). Upper part (a): behavior of $D(E_F)$ as a function of interaction strength.

a steep drop at zero. Thus in this simple case the intra-atomic d-electron interaction produces a paramagnetic insulator rather than an itinerant ferromagnet as would be the case according to the modified Stoner theory of Sec. III (see Fig. 3, bottom).

D. Body-centered cubic, $n = 7$

This is the first situation where the possible maximum of three spinband pairs is partially occupied. Again the lower bands (1,2) and (3,4) are completely filled. For $U = 0$, (5,6) and (9,10) are already nearly empty or nearly full, whereas (7,8) are half filled. This would imply five variational parameters which is numerically inconvenient. However, considering the behavior of previous cases one can safely assume that (5,6) and (9,10) will not split. Therefore in the minimization procedure we allowed only for a splitting of the half filled (7,8) bands. That leaves us again with three variational parameters. Figure 7

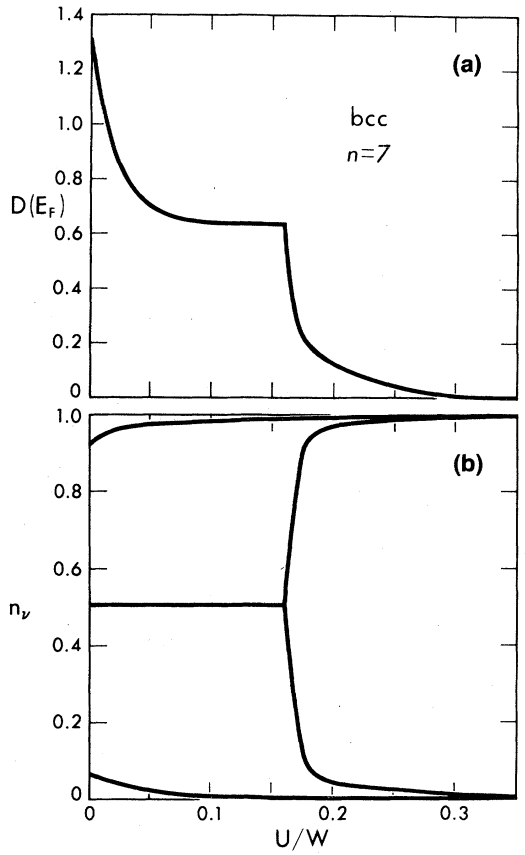

FIG. 7. Body-centered cubic, $n=7$. Lower part (b): occupation numbers for the three spinband pairs $\nu=(5,6)$ (upper curve), (7,8) (middle curves), and (9,10) (lower curve). Upper part (a): corresponding density of states.

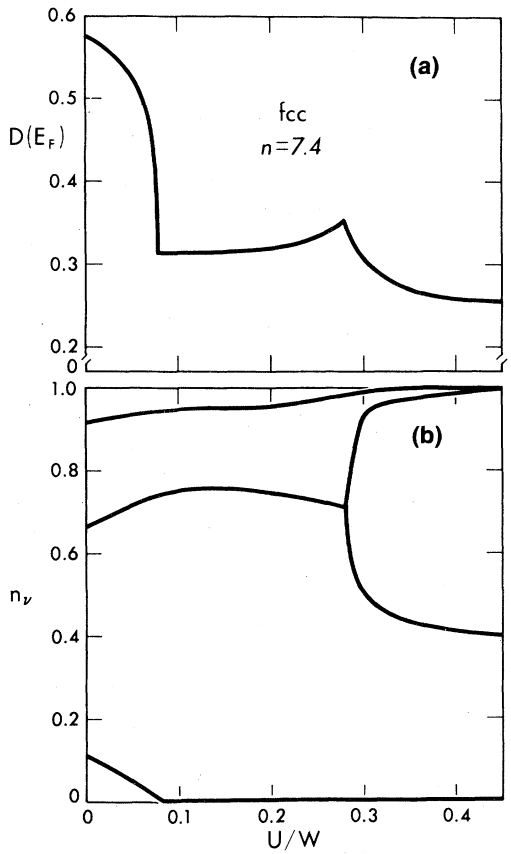

FIG. 8. Face-centered cubic, $n=7.4$. Lower part (b): occupation of the spinband pairs $\nu=(5,6)$, (7,8), and (9,10). Upper part (a): behavior of $D(E_F)$ as a function of interaction strength.

shows that (5,6) and (9,10) are quickly filled or emptied as $(U/W)\simeq 0.1$ whereas (7,8) stays approximately half filled. Correspondingly $D(E_F)$ drops to a plateau at $(U/W)=0.1$. Only at $(U/W)\simeq 0.16$ a transition to a ferromagnetic state takes place where the (7,8) pair splits and its components become either full or empty. Consequently $D(E_F)$ drops to zero. Thus we finally obtain a ferromagnetic insulator.

E. Face-centered cubic, $n=7.4$

For $U=0$ the situation is similar to the previous one, though less symmetric (Fig. 8). For the same reason as before only the (7,8) pair is allowed to split leaving us with three variational parameters. For $(U/W)<0.1$ the (9,10) bands are quickly emptied leading to an increased occupation of the lower (5,6) and (7,8) pairs. Again a steep decrease in $D(E_F)$ is the consequence. Further increase of (U/W) leads to a slow filling of the (5,6) pair. However since (5,6) is already empty, the occupation of (7,8) has to decrease again, producing a flat maximum in its occupation number and leading to a slight increase in $D(E_F)$. For $(U/W)\simeq 0.28$, however, the spin degeneracy of (7,8) is destroyed, leaving us with a finite $D(E_F)$. This means we end up with a metallic and ferromagnetic ground state.

Altogether we can classify several types of ground states for large (U/W), depending on the d-band occupation n:

1. Even integer n (case C): No ferromagnetic splitting occurs, with increasing U the bands are emptied or filled in spin-degenerate pairs, finally producing a nonmagnetic insulator.

2. Odd integer n (case D): First spinbands are emptied in pairs leaving one half filled pair which finally shows complete removal of spin degeneracy, leading to an insulating ferromagnet.

3. Noninteger n (cases A, B, E): Again filling and emptying of subbands occurs in spin-degenerate pairs until one pair is left which is more than half or less than half filled. Finally this pair shows ferromagnetic splitting leaving one still partly occupied spinband and therefore a finite density of states. This describes a metallic ferromagnet.

V. CONCLUSIONS

In our model calculations we have shown that in a fivefold-degenerate d band the intra-atomic electron interaction can lead to a more general ground state than the (generalized) Stoner model would predict. This is due to the possibility of independently changing the ten spinband occupation numbers in order to minimize the total energy. The type of ground state which develops for increasing (U/W) depends in a simple way on n, the total number of d electrons. Specifically, our calculations have shown that for a degenerate band the Hubbard interaction can lead to a reduction of $D(E_F)$ already for small values of (U/W); the resulting state is paramagnetic. This is due to the expulsion of subbands crossing the Fermi level. Such a mechanism could in principle explain the low conductivity observed in manganese which would be closely described by the case $n=6$ in our discussions of Sec. IV. Of course in our model, which does not allow for a possible breaking of the unit cell symmetry, we cannot account for the observed antiferromagnetic ground state of α-Mn which anyway has a more complicated structure than body-centered cubic. Even if we cannot make a direct comparison with experimental data, our model calculations show clearly that the usual way of neglecting d-band degeneracy in discussing itinerant magnetism is a strong oversimplification.

In conclusion, we should emphasize that the intra-atomic correlation energies may result in electronic changes similar in principle to those found in metal-insulator transitions.[4,22] Although some of the effects (those compatible with the originally assumed crystal structure and electronic ground state symmetry) are automatically included in self-consistent band-structure calculations, if the band shifting away from the Fermi level requires a change in symmetry the effects discussed here cannot be assimilated into the normal band-structure methods. Manganese with its complicated structures is once again the most suggestive metal to use to explore these phenomena in detail.

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