# Electron correlation in the narrow-band model for disordered ferromagnetic alloys*

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The ferromagnetism of a random disordered substitutional binary alloy described by the narrow-energy-band model of Hubbard is discussed within the framework of the coherent-potential approximation with strong correlation effects included. The treatment of Coulomb correlations used is an improved version of the first Hubbard approximation which seems to adequately describe those correlation effects that have a major influence on the stability of the ferromagnetic phase for large intra-atomic Coulomb repulsion. Disorder is considered in the site-diagonal terms of the Hubbard model. Numerical illustrations are presented which describe the ferromagnetic solutions in terms of the component magnetizations and component densities of states as functions of electron concentration in the band for several cases of disorder and alloy compositions. In these examples the intra-atomic Coulomb repulsion is assumed to be infinite. Comparisons are made with results obtained using a Coulomb repulsion of the order of the bandwidth treated by the Hartree-Fock approximation. One finds that results are qualitatively similar for small electron concentrations and the examples detail the differences at larger concentrations. Finally a brief discussion with respect to experiment is made.

## I. INTRODUCTION

Itinerant magnetism of disordered substitutional alloys has been discussed[1] in recent years within the framework of the coherent-potential approximation (CPA).[2,3] The CPA provides a promising approach for nondilute narrow-band magnetic alloys, and there have been practical calculations[4-7] which show reasonable agreement with experiments on ferromagnetic and enhanced paramagnetic alloys. However, in these calculations Hartree-Fock or random-phase approximations were used which ignore the strong intra-atomic Coulomb correlations present in narrow energy bands. Some attention has already been given to the problem of strong correlations in disordered alloys,[8,9] but it can be argued that the approximations used in these discussions are too restrictive to ferromagnetism and therefore do not properly describe the effects of disorder on ferromagnetism within the CPA. It is the aim of the present investigation to reexamine this problem using an approximate treatment of correlations more favorable to ferromagnetism.[10]

The model usually employed to describe narrow-band alloys is the Hubbard model,[11] where the atomic level and intra-atomic Coulomb repulsion parameters may depend on the type of atom at the given lattice site. For a single narrow band this model is represented by the Hamiltonian

$$H = \sum_{\substack{i,j,\sigma \\ (i \neq j)}} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_{i,\sigma} \epsilon_i n_{i\sigma} + \frac{1}{2}\sum_{i,\sigma} I_i n_{i,\sigma} n_{i-\sigma} , \qquad (1)$$

which is here written in second-quantized form us-ing a Wannier basis. In the case of a binary alloy of the type $A_x B_{1-x}$, the atomic-level energy $\epsilon_i$ and the intra-atomic Coulomb repulsion parameter $I_i$ take on values $\epsilon_A$ or $\epsilon_B$ and $I_A$ or $I_B$ depending on whether the $i$th site is occupied by an $A$ or $B$ atom. The transfer term is assumed independent of the types of atoms on the $i$ and $j$ sites.

In the initial treatment by Roth,[12] where effects of disorder on ferromagnetism were discussed, and in the extensive treatments by Hasegawa and Kanamori[4] and Levin et al.,[5] a local Hartree-Fock approximation was made for the Coulomb repulsion. This corresponds to replacing the model Hamiltonian of Eq. (1) by

$$H^{(HF)} = \sum_{\substack{i,j,\sigma \\ (i \neq j)}} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_{i,\sigma} (\epsilon_i + I_i \langle n_{i-\sigma} \rangle) n_{i\sigma} , \qquad (2)$$

where $\langle n_{i\sigma} \rangle$, the average electron number with spin $\sigma$ at the $i$th site, is determined self-consistently such that the dependence on the site is only on the type of atom occupying this site. Since $H^{(HF)}$ is a one-electron Hamiltonian with site-diagonal disorder the application of the CPA is straightforward. However, the Hartree-Fock approximation is justified only if the Coulomb repulsion is weak. When the Coulomb repulsion is strong, as usually assumed for narrow bands, correlations play a crucial role in determining the electronic properties.

The treatment of strong correlations in disordered alloys is a very difficult problem. As a reasonable first attempt one tries to exploit, as in the case of the Hartree-Fock treatment, the simplicity of the CPA as formulated for one-electron Hamil-

tonians with site-diagonal disorder. Several of the approximations used to treat correlations in the Hubbard model are well suited for this scheme. These treatments are characterized by the one-electron Green's function in the Wannier representation $G_{ij}^\sigma(\omega)$ being determined by an equation of the form

$$G_{ij}^\sigma(\omega) = g_i^\sigma(\omega)\, \delta_{ij} + g_i^\sigma(\omega) \sum_{l \neq i} t_{il} G_{lj}^\sigma(\omega), \qquad (3)$$

where $g_i^\sigma(\omega)$, the "$i$th-site atomic Green's function," depends only on the type of atom occupying the $i$th site. The correlations are taken into account by $g_i^\sigma(\omega)$. Although not exact for the Hubbard model, the form of Eq. (3) is suggested by the intra-atomic character of the correlations. Examples for $g_i^\sigma(\omega)$ are as follows:

(a) First Hubbard approximation[11]:

$$g_i^\sigma(\omega) = \frac{1 - \langle n_{i-\sigma}\rangle}{\omega - \epsilon_i} + \frac{\langle n_{i-\sigma}\rangle}{\omega - \epsilon_i - I_i}. \qquad (4)$$

(b) Alloy-analogy approximation of Hubbard (without resonance broadening)[13]:

$$g_i^\sigma(\omega) = \frac{1}{\omega - \epsilon_i - \Delta\epsilon_i^\sigma(\omega)}, \qquad (5)$$

where

$$\Delta\epsilon_i^\sigma(\omega) = \frac{I_i \langle n_{i-\sigma}\rangle}{1 - [I_i - \Delta\epsilon_i^\sigma(\omega)]G_{ii}^\sigma(\omega)}. \qquad (6)$$

(c) Improved first Hubbard approximation $(I_i \gg t_{ij})$[14-19]:

$$g_i^\sigma(\omega) = \frac{1 - \langle n_{i-\sigma}\rangle}{\omega - \epsilon_i - \langle n_{i-\sigma}\rangle W_{i-\sigma}}$$
$$+ \frac{\langle n_{i-\sigma}\rangle}{\omega - \epsilon_i - I_i - (1 - \langle n_{i-\sigma}\rangle)W_{i-\sigma}}, \qquad (7)$$

where

$$\langle n_{i\sigma}\rangle(1 - \langle n_{i\sigma}\rangle)W_{i\sigma} = -\sum_{j \neq i} t_{ij}[\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle$$
$$- \langle (c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}c_{i\sigma})n_{i-\sigma}\rangle]. \qquad (8)$$

For comparison the Hartree-Fock approximation is obtained with

$$g_i^\sigma(\omega) = \frac{1}{\omega - \epsilon_i - I_i\langle n_{i-\sigma}\rangle}. \qquad (9)$$

When Eq. (3) is rewritten in terms of an effective atomic-level energy $\tilde{\epsilon}_{i\sigma}(\omega)$ defined by

$$g_i^\sigma(\omega) = \frac{1}{\omega - \tilde{\epsilon}_{i\sigma}(\omega)}, \qquad (10)$$

one obtains the equation

$$\omega\, G_{ij}^\sigma(\omega) = \delta_{ij} + \sum_{l \neq i} t_{il} G_{lj}^\sigma(\omega) + \tilde{\epsilon}_{i\sigma}(\omega)\, G_{ij}^\sigma(\omega). \qquad (11)$$

The disorder associated with $\tilde{\epsilon}_{i\sigma}(\omega)$ can be treated within the framework of the usual CPA. The only new feature is the energy dependence of $\tilde{\epsilon}_{i\sigma}(\omega)$ which comes from the inclusion of correlations. Of course the success of the scheme depends on how adequately correlation effects are approximated by $\tilde{\epsilon}_{i\sigma}(\omega)$.

Fukuyama and Ehrenreich[8] have investigated strong correlations in disordered alloys using the CPA with the alloy-analogy approximation of Hubbard. The first Hubbard approximation has been used with the CPA in the work of Esterling and Tahir-Kheli[9] where the further complication of disorder in the transfer term was considered. In the case of the ordered Hubbard model, ferromagnetism is not generally possible within these approximations and this result remains unchanged with the introduction of disorder described by the CPA. Hence both these approximate treatments of correlations are probably inadequate for a discussion of the magnetic properties of narrow-band alloys. It has been argued that they are too restrictive to ferromagnetism.[14,21] In particular, as pointed out by Harris and Lange,[14] there are spin-dependent terms which do not appear in the Hubbard approximations that make ferromagnetism more favorable.

In the present investigation we treat correlations within the approximation we have called the improved first Hubbard approximation. It is appropriate to the case where the Coulomb repulsion is large compared with the bandwidth. As seen by comparing Eq. (7) with Eq. (4), this approximation differs with the first Hubbard approximation by having the $W_{i-\sigma}$ terms. These produce spin-dependent band shifts, the existence of which was indicated by Harris and Lange. The approximation is very similar to ones by Roth[15] and Tahir-Kheli and Jarrett[16] which are based on conserving the first few moments of the spectral function of the one-electron Green's function. The only difference is the neglect of certain terms appearing in those treatments which are inconsistent with the single-site character required by Eq. (3). A full discussion leading to Eqs. (3), (7), and (8) has been given by Faulkner and Schweitzer.[17]

The zero-temperature magnetic properties of the Hubbard model in the ordered case have been discussed by Meyer and Schweitzer[19] using this improved first Hubbard approximation in the limit of infinite Coulomb repulsion. The results obtained for the occurrence of ferromagnetism were reasonable extrapolations of the exact results of Nagaoka[21] for the nearly-half-filled band to arbitrary electron concentrations. These results are also in agreement with the recent treatment by Yang[22] based on a perturbation scheme. It therefore appears that this approximation provides an acceptable treatment

when $I$ is very large for the correlation effects which have a major influence on the stability of the ferromagnetic phase.

In the present application to ferromagnetism in disordered alloys where the disorder is treated within the CPA, we are primarily interested in a qualitative understanding of the effects of including correlation. We consider a model binary alloy with random disorder and treat in detail three special cases. The first case is where the disorder in the atomic-level energies is so large that the electrons are completely excluded from sites occupied by atoms of one type. Furthermore strong intra-atomic Coulomb repulsion prohibits double occupancy of the accessible sites. In the second case the disorder in the atomic-level energies is not so large and the Coulomb repulsion is assumed negligible on one type of sites. This is just the Wolff[23] model for localized magnetic moments in nonmagnetic host metals generalized to concentrated alloys. The third case considered assumes strong Coulomb repulsion on all sites. Solutions for the component magnetizations in the ferromagnetic state are obtained and representative partial densities of states are shown. For comparison Hartree-Fock results are also obtained with the Coulomb repulsion equal to the bandwidth.

The general plan of the paper is as follows. Section II gives the basic CPA formalism as generalized to treat ferromagnetic alloys with correlation effects included. The results of our numerical calculations for the three special cases are presented in Sec. III, and conclusions are summarized in Sec. IV. Also in Sec. IV there is a brief discussion with regard to experimental results for ferromagnetism in the pyrite solid solutions $Co_xFe_{1-x}S_2$ and $Ni_xCo_{1-x}S_2$.

## II. APPLICATION OF CPA

We adopt the single-band Hubbard Hamiltonian, Eq. (1), as the model for a disordered substitutional magnetic alloy $A_xB_{1-x}$. Within the treatment of Coulomb correlations considered here, the one-electron Green's function in the Wannier representation satisfies Eq. (11) for a given configuration of $A$ and $B$ atoms. The effective atomic-level energy $\tilde{\epsilon}_{i\sigma}(\omega)$ appearing in Eq. (11) is to be determined such that it takes a value $\tilde{\epsilon}_{A\sigma}(\omega)$ or $\tilde{\epsilon}_{B\sigma}(\omega)$, depending on whether the $i$th site is occupied by an $A$ or $B$ atom.

The sites are assumed to be occupied in a random way with concentrations $x$ and $1-x$ for $A$- and $B$-type atoms, respectively. In the CPA[2,3] the configuration-averaged Green's function $\bar{G}_k^\sigma(\omega)$ in the Block representation is approximated by

$$\bar{G}_k^\sigma(\omega) = \frac{1}{\omega - \epsilon_k - \Sigma_\sigma(\omega)}, \qquad (12)$$

where

$$\epsilon_k = N^{-1} \sum_{\substack{i,j \\ (i \neq j)}} t_{ij} e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)} \qquad (13)$$

and the coherent potential $\Sigma_\sigma(\omega)$ is determined self-consistently by the requirement that the single-site $T$ matrix for scattering relative to the coherent-potential medium is to vanish when configuration averaged. Thus the CPA condition for $\Sigma_\sigma(\omega)$ is

$$x\frac{\tilde{\epsilon}_{A\sigma}(\omega) - \Sigma_\sigma(\omega)}{1 - [\tilde{\epsilon}_{A\sigma}(\omega) - \Sigma_\sigma(\omega)]F_\sigma(\omega)}$$
$$+ (1-x)\frac{\tilde{\epsilon}_{B\sigma}(\omega) - \Sigma_\sigma(\omega)}{1 - [\tilde{\epsilon}_{B\sigma}(\omega) - \Sigma_\sigma(\omega)]F_\sigma(\omega)} = 0, \qquad (14)$$

where

$$F_\sigma(\omega) = F^{(0)}[\omega - \Sigma_\sigma(\omega)], \qquad (15)$$

with

$$F^{(0)}(\omega) = N^{-1}\sum_k \frac{1}{\omega - \epsilon_k} = \int_{-\infty}^{+\infty} \frac{\rho^{(0)}(\epsilon)}{\omega - \epsilon} d\epsilon, \qquad (16)$$

$\rho^{(0)}(\epsilon)$ being the density of states associated with $\epsilon_k$. The alloy density of states $\rho_\sigma(\epsilon)$ is given by

$$\rho_\sigma(\epsilon) = -\frac{1}{\pi}N^{-1}\sum_k \text{Im}\bar{G}_k^\sigma(\epsilon + i0^+)$$
$$= -\frac{1}{\pi}\text{Im}F_\sigma(\epsilon + i0^+). \qquad (17)$$

It is possible to decompose $\rho_\sigma(\epsilon)$ into partial densities of states associated with the $A$ and $B$ atoms:

$$\rho_\sigma(\epsilon) = x\rho_{A\sigma}(\epsilon) + (1-x)\rho_{B\sigma}(\epsilon). \qquad (18)$$

To evaluate $\rho_{R\sigma}(\epsilon)$, $R = A, B$, one considers an atom of type $R$ embedded in the coherent-potential medium at some site. Then the local Green's function in the Wannier representation for that site is easily determined to be

$$G_R^\sigma(\omega) = \frac{F_\sigma(\omega)}{1 - [\tilde{\epsilon}_{R\sigma}(\omega) - \Sigma_\sigma(\omega)]F_\sigma(\omega)}, \qquad R = A, B. \qquad (19)$$

Thus the component densities of states are just

$$\rho_{R\sigma}(\epsilon) = -\frac{1}{\pi}\text{Im}G_R^\sigma(\epsilon + i0^+), \qquad R = A, B \qquad (20)$$

and the average electron number with spin $\sigma$ at $A$ and $B$ sites at zero temperature is

$$n_{R\sigma} = \int_{-\infty}^{\epsilon_F} \rho_{R\sigma}(\epsilon)d\epsilon, \qquad R = A, B \qquad (21)$$

where $\epsilon_F$ is the Fermi energy determined by the total electron number.

To complete the formalism we must give the prescription for the self-consistent determination of the effective atomic-level energies $\tilde{\epsilon}_{A\sigma}(\omega)$ and $\tilde{\epsilon}_{B\sigma}(\omega)$.

Equation (10) defines $\tilde{\epsilon}_{i\sigma}(\omega)$ in terms of the "$i$th-site atomic Green's function" $g_i^\sigma(\omega)$, which in the improved first Hubbard approximation is given by Eqs. (7) and (8). When using this approximation we will for simplicity restrict our discussion to the limiting case where the Coulomb repulsion on the site is infinite. In that case ($I_i = \infty$)

$$\tilde{\epsilon}_{i\sigma}(\omega) = \frac{\epsilon_i + \langle n_{i-\sigma}\rangle (W_{i-\sigma} - \omega)}{1 - \langle n_{i-\sigma}\rangle}, \tag{22}$$

with

$$\langle n_{i\sigma}\rangle(1 - \langle n_{i\sigma}\rangle)W_{i\sigma} = -\sum_{j\neq i} t_{i\sigma}\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle. \tag{23}$$

The simplification seen in these expressions is the result of two electrons on the $i$th site being rigorously forbidden when $I_i$ is infinite.

The usual Green's-function techniques[24] yield

$$\sum_{j\neq i} t_{ij}\langle c_{i\sigma}^\dagger c_{j\sigma}\rangle = -\frac{1}{\pi}\int_{-\infty}^{\epsilon_F} d\epsilon \,\mathrm{Im}\left(\sum_{j\neq i} t_{ij}\, G_{ji}^\sigma(\epsilon + i0^+)\right) \tag{24}$$

$$= -\frac{1}{\pi}\int_{-\infty}^{\epsilon_F} d\epsilon \,\mathrm{Im}\{[\epsilon - \tilde{\epsilon}_{i\sigma}(\epsilon + i0^+)]G_{ii}^\sigma(\epsilon + i0^+)\} \tag{25}$$

where we have used Eq. (3) to obtain the final form. Hence for use with the CPA

$$\tilde{\epsilon}_{R\sigma}(\omega) = \frac{\epsilon_R + n_{R-\sigma}(W_{R-\sigma} - \omega)}{1 - n_{R-\sigma}}, \tag{26}$$

with

$$n_{R\sigma}(1 - n_{R\sigma})W_{R\sigma} = \frac{1}{\pi}\int_{-\infty}^{\epsilon_F} d\epsilon$$
$$\times \mathrm{Im}\{[\epsilon - \tilde{\epsilon}_{R\sigma}(\epsilon + i0^+)]G_R^\sigma(\epsilon + i0^+)\}, \tag{27}$$

when the Coulomb repulsion on the sites occupied by $R$-type atoms is infinite. For comparison the Hartree-Fock approximation for arbitrary $U_R$ is described by

$$\tilde{\epsilon}_{R\sigma}^{\mathrm{HF}} = \epsilon_R + U_R n_{R-\sigma}. \tag{28}$$

For a given choice of parameters $x$, $\epsilon_F$, $\epsilon_A$, $\epsilon_B$, $U_A$, $U_B$, and $F^{(0)}(\omega)$ associated with the band structure $\epsilon_k$, one must solve Eq. (21) self-consistently for $n_{A\sigma}$ and $n_{B\sigma}$ for both spin orientations. This involves the simultaneous self-consistent determination of the coherent potential $\Sigma_\sigma(\omega)$ by Eq. (14) and, in our treatment of strong correlations, the quantities $W_{A\sigma}$ and $W_{B\sigma}$ by Eq. (27). For an arbitrary density of states $\rho^{(0)}(\epsilon)$, the solution of this set of equations may become formidable. Since we are interested in qualitative aspects rather than applications to specific alloys, we shall assume the semielliptical band considered in Ref. 3:

$$\rho^{(0)}(\epsilon) = \begin{cases} (2/\pi)(1 - \epsilon^2)^{1/2}, & |\epsilon| \leq 1 \\ 0, & |\epsilon| > 1 \end{cases} \tag{29}$$

where the energy is expressed in units of one-half the bandwidth. For this density of states

$$F^{(0)}(\omega) = 2[\omega - (\omega^2 - 1)^{1/2}]. \tag{30}$$

With this particular $F^{(0)}(\omega)$ it is easy to explicitly evaluate $\Sigma_\sigma(\omega)$ as determined by Eq. (14) in terms of the $\tilde{\epsilon}_{R\sigma}(\omega)$ quantities. In practice one evaluates $F_\sigma(\omega)$ directly; the procedure is discussed in detail in Ref. 3. The remaining self-consistency conditions are solved numerically.

The numerical procedure was a fixed-point iteration scheme. One notes that in calculating the set of quantities

$$\xi_\sigma = \{n_{A\sigma}, n_{B\sigma}, n_{A\sigma}(1 - n_{A\sigma})W_{A\sigma}, n_{B\sigma}(1 - n_{B\sigma})W_{B\sigma}\} \tag{31}$$

one needs only the corresponding set $\xi_{-\sigma}$. The equations are thus of the form

$$\xi_\sigma = \mathcal{F}_\sigma(\xi_{-\sigma}). \tag{32}$$

Starting with an initial guess, the up- and down-spin quantities were calculated alternately until the absolute value of the difference between two successive iterates was less than $10^{-5}$. This termination criterion was empirically determined so as to give a consistent accuracy of three decimal places for the quantities in the $\xi_\sigma$ set. For the Hartree-Fock calculations $\xi_\sigma$ consists of $n_{A\sigma}$ and $n_{B\sigma}$ only.

In Sec. III we present some results from calculations made within our treatment of strong correlations. For comparison results using the Hartree-Fock treatment with Coulomb repulsion equal to the bandwidth are also presented.

## III. NUMERICAL ILLUSTRATIONS

In order to illustrate the effects of disorder and strong correlations on the ground-state magnetic properties of the Hubbard model we shall consider in some detail three special cases. These cases are distinguished by the choices for the parameters $\delta = \epsilon_B - \epsilon_A$, $I_A$, and $I_B$. We are primarily interested in the occurrence and character of the ferromagnetic solutions in the presence of disorder treated within the CPA when strong Coulomb correlations are included by means of the improved first Hubbard approximation. In particular, we have studied component magnetizations and component densities of states as functions of the electron concentration in the band for several values of $x$, the alloy concentration parameter. Although all the results presented are from calculations which use the simple density of states $\rho^{(0)}(\epsilon)$ of Eq. (29), we shall indicate what these results suggest for more general band shapes.

In the treatment of strong correlations by means of the improved first Hubbard approximation we have in every case assumed an infinite Coulomb repulsion. This restriction should not significantly diminish the physical character of the results since

one expects these results will be representative of the situation where the ratio of the bandwidth to the Coulomb repulsion is small. However, there is one difference between an infinite Coulomb repulsion and a large but finite Coulomb repulsion which is very important for the magnetic properties. For the ordered Hubbard model a nearly-half-filled band will have the antiferromagnetic state as the stable phase relative to the ferromagnetic for a large but finite Coulomb repulsion. This instability of the ferromagnetic state does not necessarily occur at infinite $I$ according to the Nagaoka results.[21] This situation should not change with disorder provided there is a large Coulomb repulsion at all sites. However, in the present discussion we only consider spatially uniform solutions.

### Case A:   $\delta = \epsilon_B - \epsilon_A \gg 1$

When the disorder in the atomic-level energies is large compared to the bandwidth of $\rho^{(0)}(\epsilon)$, the alloy density of states splits into two subbands, one localized at $\epsilon_A$ and the other at $\epsilon_B$. If the Fermi energy lies in the lower $\epsilon_A$ band the $B$ sites will be unoccupied and will correspond to excluded volumes in the crystal. This case has been considered by Roth[12] using the Hartree-Fock approximation for the Coulomb repulsion, and by Fukuyama and Ehrenreich[8] using the Hubbard alloy-analogy approximation with the CPA to treat the disorder. Fukuyama and Ehrenreich found no ferromagnetic solutions [their result is independent of $\rho^{(0)}(\epsilon)$]. Here we contrast the results we obtain using the improved first Hubbard approximation with the Hartree-Fock results.

For energies near $\epsilon_A$ the CPA condition for $\Sigma_\sigma(\omega)$ given by Eq. (14) reduced to

$$\Sigma_\sigma(\omega) = \tilde{\epsilon}_{A\sigma}(\omega) = \frac{1-x}{F_\sigma(\omega)} \qquad (33)$$

when $\delta = \epsilon_B - \epsilon_A \gg 1$. Then for the model density of states $\rho^{(0)}(\epsilon)$ of Eq. (29) one easily finds

$$F_\sigma(\omega) = 2([\omega - \tilde{\epsilon}_{A\sigma}(\omega)] - \{[\omega - \tilde{\epsilon}_{A\sigma}(\omega)]^2 - x\}^{1/2}). \qquad (34)$$

This yields for the component density of states associated with the $A$ sites

$$\rho_{A\sigma}(\epsilon) = (2/\pi x)\{x - \lceil \epsilon - \tilde{\epsilon}_{A\sigma}(\epsilon)\rceil^2\}^{1/2}, \qquad (35)$$

where $\tilde{\epsilon}_{A\sigma}(\epsilon)$ is the effective atomic-level energy. In the Hartree-Fock approximation $\tilde{\epsilon}_{A\sigma}(\omega)$ is given by Eq. (28) while in the improved first Hubbard approximation with $I_A$ infinite it is given by Eq. (26). This CPA result for $\rho_{A\sigma}(\epsilon)$ is seen to differ with the density of states for the ordered $A$-type Hubbard model by having its width narrowed by a factor $x^{1/2}$ while keeping the same normalization.

The ferromagnetic solutions obtained as one varies the Fermi energy across the band are shown in Fig. 1, where the average moment of an $A$ atom,
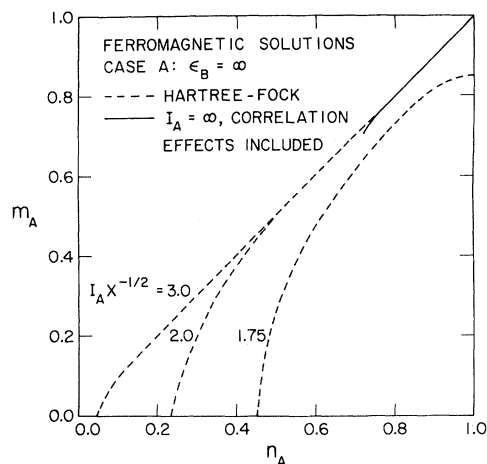


FIG. 1. Magnetization as a function of electron concentration where $\epsilon_B \gg \epsilon_A$ so that electrons are excluded from the $B$ sites.

$$m_A = n_{A\uparrow} - n_{A\downarrow}, \qquad (36)$$

is plotted as a function of the average electron concentration for an $A$ site,

$$n_A = n_{A\uparrow} + n_{A\downarrow}. \qquad (37)$$

The dashed curves are Hartree-Fock results for various values of $I_A x^{-1/2}$, which is the single parameter that characterizes the solutions in the Hartree-Fock treatment of the Coulomb repulsion. These solutions can be extended to $n_A = 2$ by noting that the curves must be symmetric about $n_A = 1$. For $I_A x^{-1/2} < \pi/2$ there are no ferromagnetic solutions. The solutions obtained when correlation effects are included within the improved first Hubbard approximation are shown by the solid curve in Fig. 1 for the case where $I_A$ is infinite. Here we restrict the range of $n_A$ such that $n_A \leq 1$ because of the infinite Coulomb repulsion. For $n_A \lesssim 0.72$ there are no ferromagnetic solutions. The onset of ferromagnetic solutions at $n_A \approx 0.72$ is discontinuous (i.e., the moment as a function of increasing $n_A$ first appears with a finite value near the saturation value) and the moment has the saturated value for $n_A \gtrsim 0.77$.

These solutions for $I_A = \infty$, where correlations are included within the improved first Hubbard approximation, are independent of the concentration $x$ for the alloy (i.e., the $m_A$ for a given $n_A$ does not depend on $x$). This result is not general to the approximation scheme but is due to our particular choice for $\rho^{(0)}(\epsilon)$, which yields a $\rho_{A\sigma}(\epsilon)$ that depends on $x$ only through a narrowing by an $x^{1/2}$ factor. Hence $x$ can be absorbed into a change in energy scale. For general band shapes there can be a nontrivial dependence on $x$; however, to the extent that the major effect of the disorder is to narrow

the band with dilution rather than to distort its shape, the solutions will be insensitive to $x$ in our approximation with $I_A$ infinite.

The discontinuous onset of ferromagnetic solutions with increasing electron concentration is also a result of our choice for $\rho^{(0)}(\epsilon)$, and is not a general feature of the approximation used to treat electron correlations. In a previous study by Meyer and Schweitzer[19] of the ordered Hubbard model which can be compared with $x = 1$ here, the onset of ferromagnetic solutions was found to be continuous for the densities of states appropriate to cubic crystals with nearest-neighbor tight-binding band structures. Clearly the magnetic properties within our treatment of correlations are quite sensitive to the form of $\rho^{(0)}(\epsilon)$. As might be expected from the magnetization results in the present case the paramagnetic susceptibility is everywhere positive and finite and hence there is no instability against an infinitesimal magnetic field perturbation. However, the ferromagnetic solution where it exists is energetically stable relative to the paramagnetic solution, indicating a first-order transition from paramagnetism to ferromagnetism with increasing electron concentration.

Finally let us contrast the results using the improved first Hubbard approximation with the Hartree-Fock results as they might be applied to an alloy system $A_x B_{1-x}$, where the $B$ sites represent excluded volume for the electrons. If we make the assumption that $n_A$ is independent of $x$ for the alloy, then $m_A$ will also be independent of $x$ in our treatment of Coulomb correlations when $I_A$ is infinite. However, in the Hartree-Fock treatment $m_A$ will increase toward its saturated value $n_A$ with decreasing value of $x$. (Of course, if $I_A$ is infinite in the Hartree-Fock treatment, $m_A$ will be saturated for all $x$.) In order to make $m_A$ insensitive to $x$ in the Hartree-Fock description one must choose $U_A$ proportional to $x^{1/2}$, which is to require $U_A$ to decrease in the same manner as the band narrows with dilution.

### Case B:  $\delta = \epsilon_B - \epsilon_A = 0.8$, $I_B = 0$

In this case the effects of disorder in both the atomic-level energies and Coulomb repulsion energies are studied. The parameter $\delta$ is chosen to be sufficiently small for the electrons to have access to both the $A$ and $B$ sites. However, since $\delta$ is comparable to half the bandwidth, the scattering is strong enough to introduce significant distortion in the component densities of states. The Coulomb repulsion on the $B$ sites is taken to be zero and thus

$$\tilde{\epsilon}_{B\sigma}(\omega) = \epsilon_B. \tag{38}$$

At the $A$ sites the Coulomb repulsion is assumed infinite when treated within the improved first Hubbard approximation. The Hartree-Fock calcula-
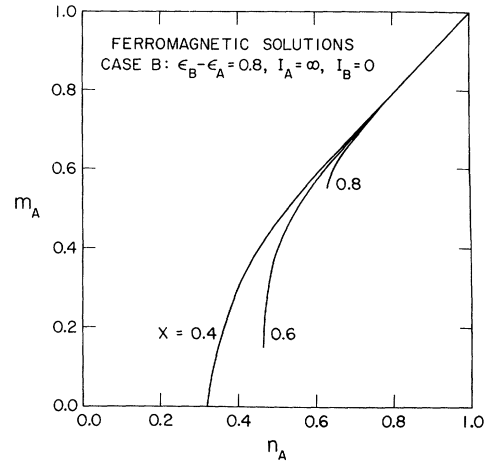


FIG. 2. Magnetization as a function of electron concentration for the $A$ sites within the improved first Hubbard approximation for various alloy compositions when $I_B = 0$ and $I_A = \infty$.

tions which we present for comparison use $I_A = 2.0$. This situation where the Coulomb repulsion is important only on the $A$ sites is the generalization to arbitrary concentrations of the Wolff[23] model for magnetic impurities in a nonmagnetic host metal.

Figure 2 shows numerical results of our treatment with $I_A = \infty$ for the $A$-site magnetization as a function of the electron density at the $A$ sites for concentrations $x = 0.4$, $0.6$, and $0.8$ of $A$ atoms. The $x = 1.0$ case is given by the solid curve of Fig. 1, which clearly also describes the ordered $A$-type crystal. One sees that the range of $n_A$ where ferromagnetic solutions exist is extended to smaller values with decreasing concentration of $A$ atoms. This is a general feature for $\epsilon_B > \epsilon_A$ which results from the distortion of the $\rho_A(\epsilon)$-component density of states. This distortion increases as $x$ decreases. In contrast, when $\epsilon_A > \epsilon_B$ the range of ferromagnetic solutions is reduced as $x$ decreases.

A more complete picture of the ferromagnetic solutions is shown in Fig. 3, where the component magnetizations and electron concentrations, as well as the alloy averages

$$\bar{m} = x\, m_A + (1 - x)\, m_B \tag{39}$$

and

$$\bar{n} = x\, n_A + (1 - x)\, n_B, \tag{40}$$

are plotted as functions of the position of the Fermi energy for the $x = 0.4$ case. Since $I_A$ is infinite the $A$ sites cannot be doubly occupied and hence $n_A = 1$ is approached as the Fermi energy moves across the band. The magnetization is almost entirely associated with the $A$ sites; however, there is a small induced magnetization on the $B$ sites. This $B$-site
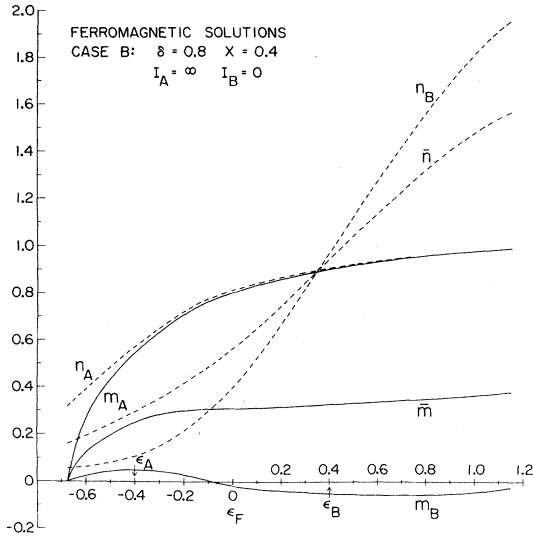
FIG. 3. Component and average magnetizations and electron concentrations as functions of the position of the Fermi energy for $x = 0.4$ using the improved first Hubbard approximation when $I_B = 0$ and $I_A = \infty$.
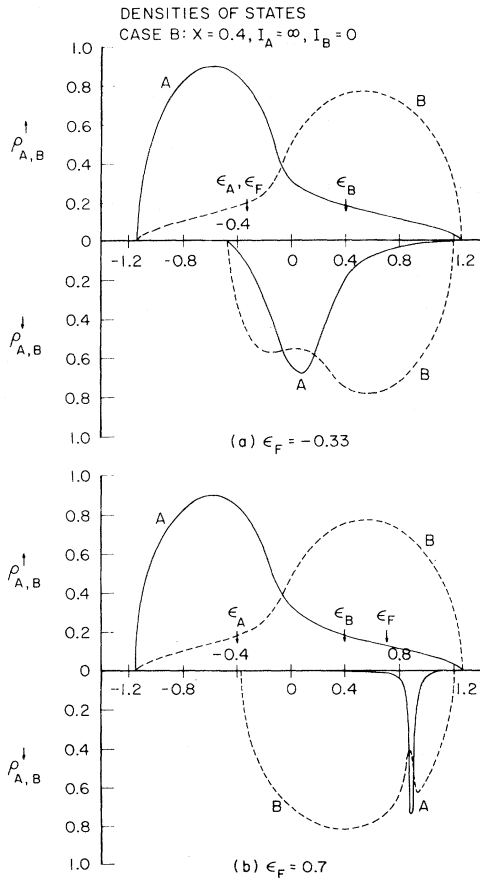
FIG. 4. Component densities of states corresponding to two solutions from Fig. 3.

magnetization is parallel to that of the $A$ sites for small $\bar{n}$ but becomes antiparallel for large $\bar{n}$ and eventually goes to zero as the band is filled ($n_A = 1$, $n_B = 2$).

In Fig. 4 we show two representative examples for the partial densities of states from the $x = 0.4$ solutions as the Fermi energy moves across the band. In Fig. 4(a) the value of $\epsilon_F$ is such that $n_A \approx 0.6$, while in Fig. 4(b) $n_A$ is very close to 1. One sees clearly the narrowing of the $A$ minority-spin band and its shift to higher energies above the Fermi energy. This increaes as the magnetization on the $A$ sites approaches saturation. The spin-dependent shift is the essential feature of our treatment of correlations that makes ferromagnetic solutions possible. The CPA treatment of disorder is responsible for the distortion of the bands from the semielliptical shape of the ordered systems to the shapes shown.

Since the occurrence of magnetic solutions depends primarily on the shape of the component density of states $\rho_{A0}(\epsilon)$, one can understand the dependence on $x$ seen in Fig. 2 in terms of the distortion from the semielliptical shape caused by the disorder. In our treatment of correlations the paramagnetic state will be more likely to be unstable against ferromagnetism at lower electron concentrations if there is a rapid increase of $\rho_A(\epsilon)$ with energy on the low-energy end and an extended tail on the high-energy end. This is just what the disorder produces when $\epsilon_B > \epsilon_A$ provided the difference is not so large as to reduce the situation to that discussed in case A. However, if $\epsilon_A > \epsilon_B$ the distortion of $\rho_A(\epsilon)$ is such as to make ferromagnetism less likely.

The Hartree-Fock treatment with $I_A = 2.0$ yields results which are in several ways quite similar to the results of our treatment of correlations with $I_A$ infinite. This is consistent with the general expectation that correlations must reduce $I_A$ effectively to a quantity of the order of the bandwidth. Figure 5 shows the ferromagnetic solutions for $x = 0.4$
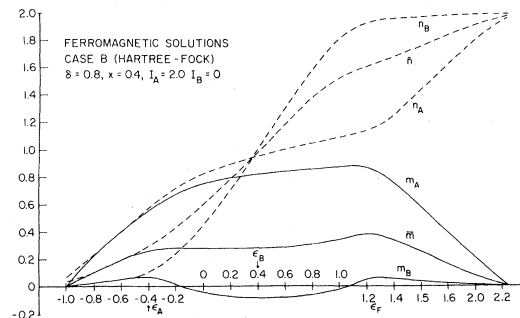
FIG. 5. Component and average magnetizations and electron concentrations as functions of the position of the Fermi energy for $x = 0.4$ using the Hartree-Fock approximation when $I_B = 0$ and $I_A = 2.0$.

DENSITIES OF STATES
HARTREE-FOCK CASE B
$X = 0.4, I_A = 2.0, I_B = 0$



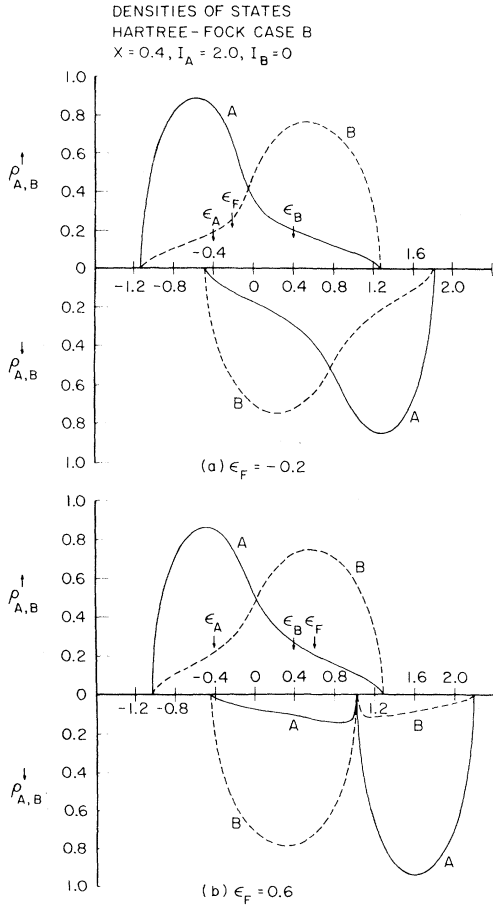(a) $\epsilon_F = -0.2$

(b) $\epsilon_F = 0.6$

FIG. 6. Component densities of states corresponding to two solutions from Fig. 5.

when the Hartree-Fock approximation is used with the CPA. The different behavior seen in Figs. 3 and 5 is primarily due to the fact that in the case where $I_A$ is infinite and correlations are included $n_A$ must approach 1 as the Fermi energy increases across the band since the states corresponding to double occupancy of the $A$ sites have been displaced to infinity. Hence, for $n_A$ not too close to 1 the two treatments yield results which are very similar for the dependence of the ferromagnetic solutions on the average electron concentration.

Representative densities of states are shown in Fig. 6 for the Hartree-Fock solutions. In contrast with the results shown in Fig. 4 there is no narrowing of the $A$ minority-spin band. The Hartree-Fock approximation gives only a rigid spin-dependent shift. However, one can see clearly in Fig. 6(b) that this shift enhances the disorder with the result that the majority- and minority-spin bands can be quite different in shape.

In the Hartree-Fock treatment the occurrence of ferromagnetic solutions is essentially determined

by the Stoner criterion $I_A \rho_A(\epsilon_F) \geq 1$, where $\rho_A(\epsilon)$ is the paramagnetic component density of states at the Fermi energy. As a result of the distortion of $\rho_A(\epsilon)$ due to the disorder the range of ferromagnetic solutions is extended to smaller $n_A$ with decreasing concentration of $A$ atoms when $\epsilon_B > \epsilon_A$, and constricted to values near $n_A = 1$ for $\epsilon_A > \epsilon_B$. Although there is little apparent relationship between the Stoner criterion and what is involved when one treats correlations within the improved first Hubbard approximation, nevertheless the results for the dependence of the ferromagnetic solutions on the concentration $x$ of $A$ atoms are qualitatively the same in both treatments for our simple model density of states.

Case C:   $\delta = \epsilon_B - \epsilon_A = 0.8, I_A = I_B$

In this example we study the effects of disorder in the atomic-level energies when there is strong Coulomb repulsion at all sites. Again for the treatment where correlations are included we assume this Coulomb repulsion to be infinite and therefore there can be no doubly occupied sites.

Figure 7 shows the ferromagnetic solutions for a concentration $x = 0.4$ of $A$-type atoms. In contrast to case B both $n_A$ and $n_B$ must approach 1 as the Fermi energy is increased across the band. Also the contribution to the magnetization from the $B$ sites is larger as expected with $I_B$ infinite, and it can be either parallel or antiparallel to the $A$-site magnetization depending on $\bar{n}$. A particularly interesting feature is the behavior of $m_B$ near $\bar{n} = 1$. Here one sees that $m_B$ is parallel to $m_A$ and is increasing rapidly as $\bar{n} = 1$ is approached. Unfortunately our numerical procedure did not permit us to follow the solutions closer to $\bar{n} = 1$ than shown. It is expected, however, that $m_B$, like $m_A$ will become saturated so that $\bar{m} = \bar{n}$ at $\bar{n} = 1$. Such a behavior is suggested by an extension of the exact results of Nagaoka which includes disorder.[25]
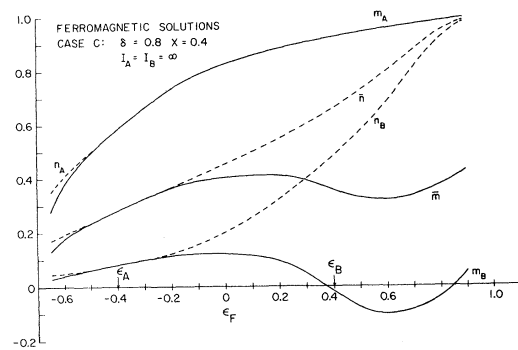


FIG. 7. Component and average magnetizations and electron concentrations as functions of the position of the Fermi energy for $x = 0.4$ using the improved first Hubbard approximation when $I_A = I_B = \infty$.

DENSITIES OF STATES
CASE C: X = 0.4, $I_A = I_B = \infty$



(a) $\epsilon_F = -0.4$

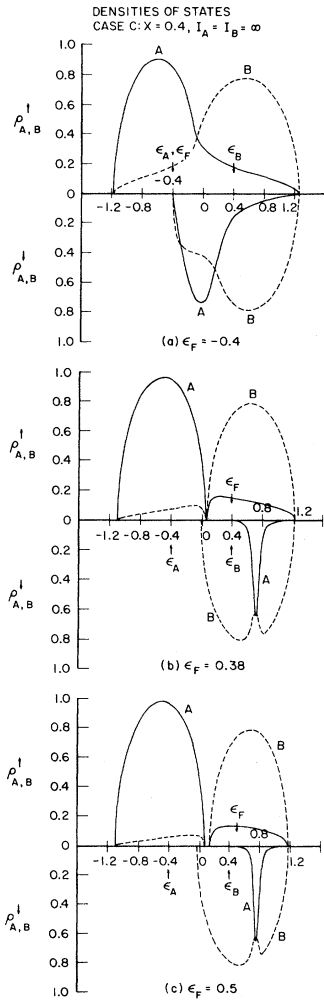(b) $\epsilon_F = 0.38$

(c) $\epsilon_F = 0.5$

FIG. 8. Component densities of states corresponding to three solutions from Fig. 7.

Another important feature seen in Fig. 7 is the existence of a range of $\bar{n}$ where $\bar{m} = \bar{n}$. This saturated region is displaced to smaller $\bar{n}$ with decreasing concentration $x$ of $A$-type atoms. We shall comment in Sec. IV on this behavior being important for the understanding of some experimental observations on itinerant narrow-band alloys.

The evolution of the component densities of states as $\epsilon_F$ increases across the band is shown in the three examples of Fig. 8. One sees the expected complicated interplay between disorder and correlation effects. These examples aid in understanding the behavior seen in Fig. 7 for the component magnetizations.

Now let us inspect the Hartree-Fock results for the same disorder in the atomic-level energies but with $I_A = I_B = 2.0$. The $x = 0.4$ solutions are shown in Fig. 9. One notes that the rather complicated curves for the component magnetizations show the

expected near symmetry between electrons on $A$ sites and holes on $B$ sites. In making a comparison with Fig. 7 one should consider only the $\bar{n} \leq 1$ solutions. There is a qualitative similarity for small $\bar{n}$ and significant deviations near $\bar{n} = 1$ as should be expected. At smaller $\bar{n}$ one finds a saturated region ($\bar{m} = \bar{n}$) similar to that found in the treatment with correlations included. However, unlike the behavior seen in Fig. 7, here $m_A$ does not remain saturated as $n_A = 1$ is approached and also the antiparallel $B$-site magnetization becomes very large. This behavior can be understood in terms of the evolution of the component densities of states as $\epsilon_F$ increases, as shown in the examples of Fig. 10. A comparison of Figs. 8 and 10 shows some of the effects of Coulomb correlations.

## IV. CONCLUSIONS

We have reexamined the problem of strong Coulomb correlations and disorder in the Hubbard model using the CPA to treat the disorder and the improved first Hubbard approximation described by Eqs. (3), (7), and (8) to treat the Coulomb correlations. Although this treatment of Coulomb correlations has several dissatisfactory features it seems to provide, when the Coulomb repulsion is large compared with the bandwidth, an adequate description of those correlation effects that have a major influence on the stability of the ferromagnetic phase relative to the paramagnetic phase. It is hoped that it provides some insights into inadequacies of the Hartree-Fock treatment.

Unfortunately this treatment involves much more calculational effort than the Hartree-Fock description, and therefore it would be quite difficult to go beyond the simple-model-alloy calculations shown. However, the examples considered here indicate that the Hartree-Fock description with an effective Coulomb repulsion of the order of the bandwidth
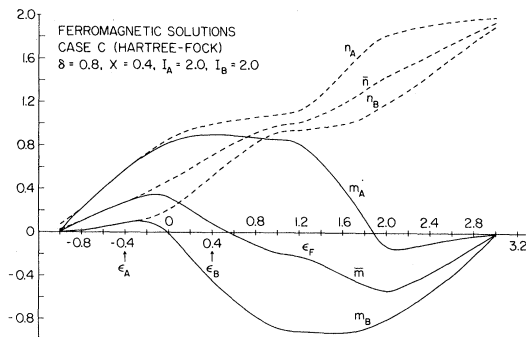


FIG. 9. Component and average magnetizations and electron concentrations as functions of the position of the Fermi energy for $x = 0.4$ using the Hartree-Fock approximation when $I_A = I_B = 2.0$.

DENSITIES OF STATES
HARTREE-FOCK CASE C
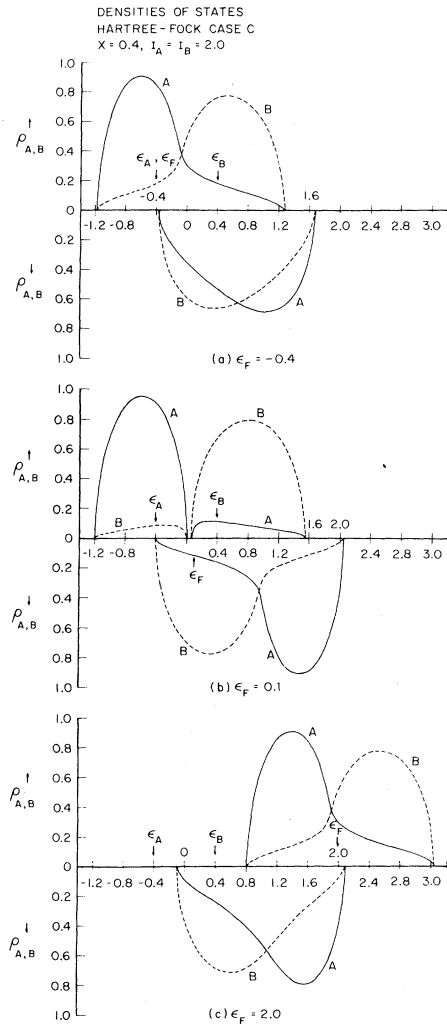X = 0.4, $I_A = I_B = 2.0$



FIG. 10. Component densities of states corresponding to three solutions from Fig. 9.

gives a very similar description for the case where the Coulomb repulsion is large compared with the bandwidth, provided the electron concentration is small. Hence our treatment suggests how to interpret the Coulomb repulsion parameter in Hartree-Fock treatments. This result is consistent with the exact low-density results of Kanamori[26] for the ordered Hubbard model.

A major effect of strong correlations is to displace the states corresponding to double occupancy of sites to higher energies making them inaccessible. This feature is missing in the Hartree-Fock description and hence it cannot properly describe the situation as $n_R \to 1$ with $I_R$ very large. Our results suggest what deviations are expected from the Hartree-Fock results. These deviations are detailed by the examples shown.

Finally let us briefly comment on a possible application of our results to experiment. The pyrite solid solutions $Co_xFe_{1-x}S_2$ and $Ni_xCo_{1-x}S_2$ can likely be described by the Hubbard model with strong intra-atomic Coulomb repulsion.[27,28] In these materials crystal fields are important and one pictures the conduction band arising solely from the doubly degenerate $d$ orbitals of $e_g$ symmetry. $FeS_2$ is a nonmagnetic semiconductor; $CoS_2$ is a ferromagnetic metal with 1 conduction electron per Co atom; and $NiS_2$ is an antiferromagnetic semiconductor with two $e_g$ electrons per Ni atom. Hence the $e_g$ electron concentration should go from 0 to 1 in $Co_xFe_{1-x}S_2$ and from 1 to 2 in $Ni_xCo_{1-x}S_2$ as $x$ is increased from 0 to 1. The semiconducting character of $NiS_2$ indicates splitting of the band due to strong Coulomb correlations.

If Hund's-rule interactions are neglected, one can use the nondegenerate-band Hubbard model with the electron concentration given by $\bar{n} = \frac{1}{2} x$ for $Co_xFe_{1-x}S_2$ and $\bar{n} = \frac{1}{2}(1 + x)$ for $Ni_xCo_{1-x}S_2$. The atomic-level parameters must be chosen such that $\epsilon_{Fe} > \epsilon_{Co} > \epsilon_{Ni}$. Then it is clear from our model calculations that there will be a tendency toward saturated ferromagnetism ($\bar{m} = \bar{n}$) as $x$ decreases in the $Co_xFe_{1-x}S_2$ alloy system and a tendency away from saturation with increasing $x$ in the $Ni_xCo_{1-x}S_2$ system. This behavior, which is seen in experiments, is found both in our treatment with correlation effects and in the Hartree-Fock treatment with the Coulomb repulsion of the order of the bandwidth. Also, as the Ni concentration in $Ni_xCo_{1-x}S_2$ increases the electron concentration approaches the half-filled band limit and therefore one expects to see a transition from ferromagnetism to antiferromagnetism at some value of $x$ since the Coulomb repulsion is large but finite. This final feature, however, is outside the scope of the solutions considered in this investigation.

These considerations suggest that the Hubbard model with disorder treated within the CPA can provide a simple explanation of the behavior seen in these alloys. A more detailed application will be presented in the future.

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