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# Theory of Ferromagnetism in Narrow-Band Solids, with Application to Experiments on $\mathrm{Co}_x\mathrm{Fe}_{1-x}\mathrm{S}_2$

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In a previous publication, ferromagnetism of the Hubbard model was studied in the infinite-interaction limit for a nearly half-filled band, using a new diagrammatic approach based on the work of Nagaoka. In this paper, the results of this previous work are shown to apply away from the nearly half-filled-band limit, in which this system was shown to be rigorously ferromagnetic in a paper by Nagaoka. As was done previously, the approach due to Nagaoka, in which one considers the motion of "holes" (i.e., sites not containing an electron) is used to obtain an expansion of the partition function in powers of inverse temperature. The approximation of keeping only contributions from those "hole" paths having electrons of one spin only is shown to be valid over a wide range of electron concentration. Using this method, the Curie temperature and magnetization are calculated and compared in detail with some transition-metal disulfide experimental systems which are simple two-band itinerant-electron systems to which this model can be shown to be applicable. To understand these systems, a discussion of their disordered nature is introduced. Comparison is also made with other narrow-band theories, including Hubbard's theory and the work of Harris and Lange.

## I. INTRODUCTION

In Ref. 1 (hereafter referred to as I), the magnetic properties of the Hubbard model[2] were discussed in the limit of interaction strength much larger than bandwidth. The theory discussed in I was shown to be valid for fcc lattices with further than near-neighbor hopping included, for a nearly half-filled band (i.e., near the limit discussed by Nagaoka[3]). In this paper, it will be argued that that theory should be valid as we move away from the limit of one electron per site.

In the infinite-interaction-strength limit, the Hubbard Hamiltonian reduces to

$$\mathcal{H}=\sum_{ij\sigma} h_{ij}\, a_{i\sigma}^{\dagger} a_{j\sigma}\,, \qquad (1)$$

where

$$a_{i\sigma}=(1-n_{i,-\sigma})c_{i\sigma}\,, \quad n_{i\sigma}=c_{i\sigma}^{\dagger}c_{i\sigma}\,.$$

where $c_{i\sigma}$ is the annihilation operator for an electron of spin $\sigma$ on lattice site $i$, and $h_{ij}$ is the hopping integral.[1,2,4] Throughout this paper Eq. (1) will be taken as our model Hamiltonian. In this model, electrons hop from site to site in such a way that there are never two electrons on a lattice site. Harris and Lange[4] discussed exact sum rules satisfied by the one-electron Green's function of this model. We will discuss our results in the light of their results in Sec. III.

Both I and Brinkman and Rice[5] discuss this model by expanding either the resolvent or the partition function in a power series in $h_{ij}$. A term of order $n$ in such an expansion was shown to be related to the number of paths of a "hole" (i.e., a lattice site not containing an electron of either spin), in which the "hole" after $n$ hops ends up on its original site and all the spins in the system are returned to their original configuration. In order to guarantee that the spin ordering is unchanged by the motion at the "hole," Brinkman and Rice[5] sum only those paths in which the "hole" retraces its steps. Such paths were shown to give the largest contribution to the first 12 orders in the expansion of the resolvent for the near-neighbor hopping in a simple cubic lattice. By doing so, they are able to sum the series exactly and thus obtain the density of states for a "hole" (or excess electron) created in an exactly half-filled band. They then use their approximation to find the electrical mobility. In I, the paths summed are those on which all electrons have the same spin. The object in I was to obtain the magnetic properties of the system. These same spin or "ferromagnetic" paths give a contribution comparable to that of the self-retracing paths summed by Brinkman and Rice for the fcc lattice with near-neighbor hopping. If more than near-neighbor hopping is included, they can be shown to dominate the higher-order terms in the expansion of the partition function in $h_{ij}/KT$, which are the most important orders for low temperatures for *close* to a half-filled band. Closer to the half-filled-band or Nagaoka limit, the magnetic properties are discussed in Ref. 6.

In Sec. II, a critical discussion is given of both these theories. It is then argued that the "ferromagnetic" path approximation should be the appropriate approximation to use away from the half-filled-band limit. In Sec. III, this approximation is compared with various other narrow-band theories. In Sec. IV, the validity of this theory for describing some experimental observations on transition-metal disulfides and transition metals is discussed.

## II. CRITICAL DISCUSSION OF BOTH THEORIES

### A. Away from Nagaoka Limit

The first six moments $A_l$ of the spectral density, which give the first six orders in the expansion of the resolvent, for a single "hole" in a half-filled band[5] have been calculated and tabulated in Table I for the fcc lattice with near-neighbor hopping. Also listed are the contributions obtained using self-retracing and "ferromagnetic" paths alone. (The work of Domb was used in compiling this table.[7]) In terms of the moments, the resolvent is given by

$$\mathrm{Tr}(\omega-\mathcal{H})^{-1}=\sum_{l=0}^{\infty} A_l \frac{h^l}{\omega^{l+1}} ,$$

where $h$ is the near-neighbor hopping matrix and $A_l$ is the $l$th-order moment, given in Table I. As is seen from this table, although the self-retracing paths work quite well for the first 12 orders for the simple cubic,[5] they fail quite badly for the fcc lattice. The ferromagnetic paths do not seem to be a much better approximation although they do give the odd-order terms that are not obtained in the self-retracing-path approximation. Some combination of these two paths would probably be the best approximation; however, it is difficult to sum both contributions analytically in such a way as to avoid overcounting. We will not be concerned with this problem in this paper, but rather with what happens as we move away from the half-filled-band limit. When the system is partly magnetized, the ferromagnetic paths start to dominate the high-order terms. When the system is 2% magnetized, higher-order terms are dominated by ferromagnetic paths as seen in Table I. The point to be made here is that results valid for a nearly half-filled band appear to be very much dependent on the lattice. The reason for the interest in the fcc lattice is that the metallic ions in transition-metal disulfides, to which we expect the results of this paper to apply, lie on an fcc lattice.[8]

As we move away from the half-filled-band limit, there are two effects which must be considered. First, as was pointed out in I, there are "hole" exchange paths. As in a normal noninteracting fermion system, their effect is to give rise to a Pauli exclusion principle for "holes." It was seen in I that these exchange paths enter with a sign $(-1)^{p+1}$, where $p$ is the number of "holes" exchanged. They thus subtract from the partition-function contributions in which more than one "hole" occupies the same state. Second, there is an indirect "hole"-"hole" interaction, which was not included in I. This interaction comes about because two holes can cross each other's paths. When this happens, certain paths that normally would be included in the expansion of the partition function must now be excluded. This happens because the second "hole," on crossing the path of the first, can change one of the spins on the path. For example, consider a "hole" which executes a certain path away from its original site and then retraces that path. If before it has retraced its path a second "hole" crosses the path and changes one of the spins, the spins will not be returned to their original configuration when the path is retraced. If there are many holes in the system, i.e., we are away from the half-filled-band limit, each "hole" will have its path crossed many times. Thus, it will be very unlikely for a "hole" to traverse a path more than once and be able to return the spins to their original state. Thus, the only paths that are allowed are the "ferromagnetic" paths. Hence, the results of I should be valid well away from the half-filled-band limit. In fact, "ferromagnetic" paths should be the dominant paths away from the nearly half-filled-band limit.

As may be inferred from I and Ref. 5, the existence of ferromagnetism is due to the fact that the "hole" bands are narrower in the paramagnetic state than in the ferromagnetic state. Thus, the "holes" near the bottom of the "hole" bands have lower energy when there is ferromagnetic ordering. When we neglect the contribution due to certain classes of paths (i.e., nonferromagnetic paths in this case), we are most likely narrowing the

TABLE I. First six moments $A_l$ of the spectral density for paramagnetic and ferromagnetic states of an fcc lattice.

| $l$ | Ferromagnetic state | Paramagnetic state | Parmagnetic state self-retracing paths only | Paramagnetic state ferromagnetic paths only | $M/N_a=0.2$ | $M/N_a=0.2$ Ferromagnetic-path approximation |
|---|---|---|---|---|---|---|
| 2 | 12 | 12 | 12 | 12 | 12 | 12 |
| 3 | 48 | 24 | 0 | 24 | 24.96 | 24.96 |
| 4 | 580 | 362 | 296 | 222 | 375.52 | 223.20 |
| 5 | 4176 | 1458 | 0 | 858 | 1558.66 | 982.66 |
| 6 | 44 892 | 14 539.5 | 7332 | 6236.5 | 15 589.96 | 7588.76 |

bands a little too much. Since excessive band narrowing increases the tendency towards ferromagnetism, we expect the results of including only ferromagnetic paths to be a slight overestimate of the tendency towards ferromagnetism (i.e., an overestimate of the Curie temperature). We know, however, that the system should order ferromagnetically for the following reason.

The partition function for those lattices considered by Nagaoka[3] is given by

$$Z = \sum_{\text{spin config}} \bar{Z} \ , \tag{2}$$

where

$$\bar{Z} = \sum_n (A_n - B_n)(\beta h)^n / n! \ , \tag{3}$$

where $A_n$ is the sum of all "hole" paths of positive sign with a total of $n$ hops and $B_n$ is the sum of all exchange paths of negative sign with a total of $n$ hops. $A_n$ and $B_n$ are functions of magnetization. For each exchange path, there is at least one nonexchange path giving the same contribution (i.e., same number of hops), namely a single "hole" following the total length of the exchange path, instead of two or more "holes" exchanging places on the path. In a state of zero magnetization, $A_n$ is noticably smaller than in the completely ferromagnetic state because there are fewer allowed paths in the nonmagnetic state (i.e., paths in which the spin configuration is returned to its original state in the end). This can be seen in Table I. From what we have said about exchange paths, $A_n - B_n$ must be smaller in a nonmagnetic than in the ferromagnetic state. Thus, there is a tendency towards ferromagnetism until the electron density becomes low enough for the results of this treatment in terms of "holes" to become meaningless. More will be said about this later in this section. For the Nagaoka (i.e., nearly half-filled-band) limit, the "holes" can lower their energy by remaining in a region in which all spins point in the same direction, and in the thermodynamic limit, these regions can be large enough to lower the "hole" energy to the energy at the bottom of the band, which is equal to the lowest "hole" energy in the ferromagnetic state. It was shown, however, in Ref. 6, that because of the "hole" exchange, the system probably still orders ferromagnetically for three-dimensional lattices. In two dimensions there is no long-range magnetic order, but there could be short-range order.[9]

To summarize, we expect the "ferromagnetic-path" approximation to be valid for roughly between a half- and a quarter-filled band, but we do not expect the approximation to be too accurate numerically in the nearly half-filled-band limit itself. For very low electron densities [for example, for less than a quarter-filled band (i.e., less than half an electron per site)], the approximation is probably also not too accurate.

### B. Numerical Results of Ferromagnetic-Path Approximation

Let us consider the results of a calculation of the magnetic properties using this approximation. In this paper, instead of restricting "holes" to paths containing electrons of the same spin, we will restrict the "holes" to paths *not having* electrons of a given spin. That is, we allow "holes" to hop onto sites containing other "holes." If the spins of the paths traversed by two such "holes" are the same, there will be an exchange collision path equivalent to this direct collision path which will cancel it. Two "holes" moving on paths of opposite spin cannot collide in the "ferromagnetic-path" approximation used here because that would mean that one path was not "ferromagnetic." Following the procedures of I, we find the following grand-cannonical partition function:

$$Q = \prod_{\vec{k}, \sigma_h} \{1 + \exp\beta[\epsilon(\vec{k})(1 - n_{-\sigma_h}) - \mu]\} \binom{N_e}{M} \ , \tag{4a}$$

where $N_e$ is the number of electrons, $n_{-\sigma} = N_{-\sigma}/N_a$, where $N_\sigma$ is the number of spin $\sigma$ electrons, and where $\sigma_h$ is the spin of the electrons on a path followed by a "hole." The methods used in I which lead to Eq. (4a) restrict the "holes" to ferromagnetic paths probabalistically. In such an approximation, we neglect damping of the single "hole" states. This problem will be discussed in Sec. IV. Equation (4a) is a mixed-connonical-grand-connonical ensemble defined as follows:

$$Q = \sum_{N_h} e^{\beta\mu N_h} Z_{N_h} \ , \tag{4b}$$

where $\mu$ is a chemical potential for the "holes." Here we sum over $N_h$ but keep $N_e$ fixed (i.e., we relax the restriction $N_h = N_a - N_e$). We then require the average $N_h$ to satisfy $N_h = N_a - N_e$. It follows from Eq. (4a) that the magnetization, susceptibility, and number of "holes" are given by

$$m = N_e \tanh\{-\tfrac{1}{4}(1/N_a) \textstyle\sum_{\vec{k}} [f(\epsilon(\vec{k})(1 - n_{-1})) - f(\epsilon(\vec{k})(1 - n_{+1}))] \beta\epsilon(\vec{k})\} \ , \tag{5a}$$

$$\chi = N_e/(KT - K\Theta) \ , \tag{5b}$$

where

$$K\Theta = \tfrac{1}{4}(N_e/N_a)(1/N_a) \textstyle\sum_{\vec{k}} \epsilon(\vec{k})^2 f'(-\epsilon(\vec{k})(1 - n_{+1})) \ ,$$

where $f(x)$ is a Fermi function, $f'(x)$ is its derivative, and

$$N_h = \sum_{\vec{k}, \sigma_h} f(-\epsilon(\vec{k})(1 - n_{-\sigma_h})) \ . \tag{5c}$$

It was shown in I that for $N_h/N_a$ less than 0.25 the high-temperature susceptibility $\chi$ does not obey a Curie-Weiss law because of the strong temperature dependence of $\Theta$. It was also shown that the Curie temperature reaches a maximum value equal to approximately 4% of the bandwidth for $N_h/N_a$

$\approx 0.25$, and falls to zero at $N_h/N_a = 0$ (i.e., a half-filled band). Let us consider $\Theta$ and $T_c$ for lower electron density. For $N_h/N_a \geq 0.4$ (i.e., $N_e/N_a \leq 0.6$), it was shown in I that $\Theta$ is independent of temperature for temperatures of the order of $T_c$. This occurs because at such "hole" densities, the "holes" form a degenerate fermion system. Then, we may replace the Fermi function by a step function for such low electron densities and temperatures. Making this approximation and using a square density of states [i.e., density of states $\rho(\epsilon)$ nonzero for $\epsilon$ between $-\Delta$ and $\Delta$, where $2\Delta$ is the bandwidth, and 0 outside this range], we may solve Eqs. (5a) and (5c) simultaneously to obtain the following relationship giving $m$ as a function of $T$ and $N_e/N_a$:

$$m = N_e \tanh \beta\Delta m \left(\frac{0.25(N_e/N_a)^2}{1-\frac{1}{2}N_e/N_a}\right) \quad . \qquad (6)$$

This is simply the magnetization in the molecular field approximation for a Heisenberg-model spin system. Then, the susceptibility above $T_c$ is Curie-Weiss and the Curie temperature is given by

$$KT_c = \tfrac{1}{4}\Delta \frac{(N_e/N_a)^2}{1-0.5N_e/N_a} \quad . \qquad (7)$$

$T_c$ goes to 0 quadratically for low electron density and increases faster than $(N_e/N_a)^2$ as the electron density increases. For near 0.60, the curve of $T_c$ vs $N_e/N_a$ no longer follows Eq. (7) but bends over and has a maximim at $N_e/N_a = 0.75$, as shown in I. The same calculation was also performed using the density of states calculated from near-neighbor tight-binding functions for a fcc lattice. The result is shown in Fig. 1. The dependence of $T_c$ on density is a little stronger and $T_c$ falls to zero for nonzero $N_e/N_a$ (at $N_e/N_a \approx 0.2$). This lattice structure is the one on which the metallic ions lie in the transition-metal disulfides to which this theory should apply. The results for $T_c$ vs $N_e/N_a$ agree qualitatively with the experimental results of Jarrett *et al.*[8] on transition-metal disulfides, which are plotted on the same graph in Fig. 2, in that both curves peak in the same place. The Curie temperature tails off, however, more rapidly in this theory than in the experiments and goes to zero when $N_e/N_a$ becomes 1. The square density of states should be appropriate because of the extremely disordered nature of the cobalt iron disulfides system.

Equation (5a) has been solved for $m$ vs $T$, using a square density of states again. The results are plotted in Fig. 3 with the experimental results of Jarrett *et al.* for $Fe_{0.75}Co_{0.25}S_2$. The magnetization versus temperature for the molecular field solution of the Heisenberg model with the saturation magnetization and $T_c$ fit to the same scale (which is what we get in the large-$U$ limit of Stoner theory) are plotted on the same graph. All three curves appear to agree with each other quite well. Thus, it appears that both Stoner theory and the present model will fit the magnetization for this mixture of compounds. (If $U$ is greater than the bandwidth, Stoner theory also gives a saturation magnetization equal to the number of electrons in the system.) The present model, in which correlations are taken as important, however, should be a better description of the Hubbard Hamiltonian when $U$ is greater than the bandwidth than is the Stoner theory (i.e., Hartree-Fock theory) in which correlations are neglected. Electron-electron correlations can only be neglected if electron-electron interactions are not too large.

As seen in Fig. 4, the magnetization-vs-$T$ curve falls below that curve for Stoner theory as we get closer to a half-filled band. Furthermore, the magnetization curve for the disulfides lies above the curve found from the Stoner theory for $N_e/N_a > 0.75$. These deviations from the present theory will be discussed in the Sec. IV.

As the density of electrons becomes small (for less than a filled band), the approximation used here does not give a total energy which goes to zero as the electron density approaches zero [i.e., the total energy in the exponent to Eq. (4a) does not go to zero]. The source of this error is the distinction made, in calculating "hole-hole" exchange effects, between spin-up and spin-down "holes" (according to the spin of the electrons on the path on which they travel). When the density of electrons

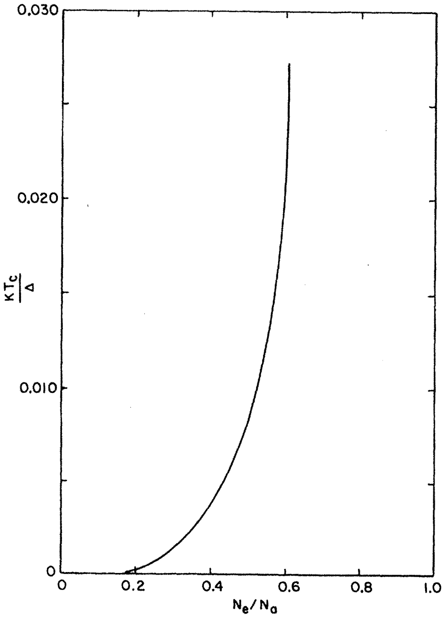

FIG. 1. $T_c$ vs $N_e/N_a$ for a fcc lattice with near-neighbor hopping for low hole density ($T_c$ in units of $\Delta/K$, where $K$ is Boltzmann's constant).

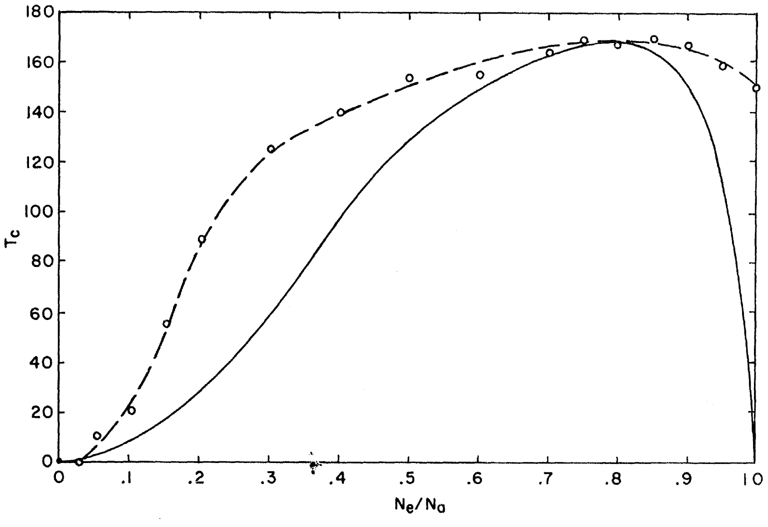

FIG. 2. $T_c$ vs $N_e/N_a$. The solid line is for a square density of states ($T_c$ in °K). Dashed line is the data of Jarrett *et al.* on the cobalt-iron disulfide system (Ref. 8).

is small, most of the "holes" move on paths which contain no electrons, which makes this distinction meaningless. Then, if we drop this distinction at low electron densities, the energy becomes

$$E=-\sum_{\vec{k}\text{ occupied by "holes"}}\epsilon(\vec{k})(1-\tfrac{1}{2}N_e/N_a)\ . \qquad (8)$$

The system is taken to be paramagnetic here. We should make a distinction, however, between spin up and spin down in sites containing electrons. We do this by treating the electrons as holes in the "hole" band and treating spin correctly for them. Then, we sum Eq. (8) over all $\vec{k}$, which gives 0, and subtract off the energy due to the electrons, each of which has an energy $\epsilon(\vec{k})(1-\frac{1}{2}N_e/N_a)$, since each electron is a hole in the "hole" band. For the electrons, however, we do have to make the distinction of spin in labeling states to calculate exchange. We thus obtain

$$E=2\sum_{\vec{k}\text{ occupied by electrons}}\epsilon(\vec{k})(1-\tfrac{1}{2}N_e/N_a)\ . \qquad (9)$$

For a square density of states, we find

$$E/N_a=-2n\Delta(1-2n). \qquad (10)$$

This is to be compared with the result of Kanamori's theory which in this limit gives[10]

$$E_{\text{Kanamori}}/N_a=-2n\Delta(1-n)\ , \qquad (11)$$

where $n=0.5N_e/N_a$. Since the energy given in Eq. (11) is smaller than the energy in the ferromagnetic state, but Eq. (10) gives about the same energy as the ferromagnetic state, we see that our approximation overestimates the tendency to ferromagnetism in this limit. Nevertheless, for greater than a quarter-filled band, we expect the results of this paper to be qualitatively correct.

### C. Simple Multiband Generalization

The methods of this paper can easily be applied to a simple multiband model of a ferromagnetic substance in the limit of strong intra-atomic Cou-

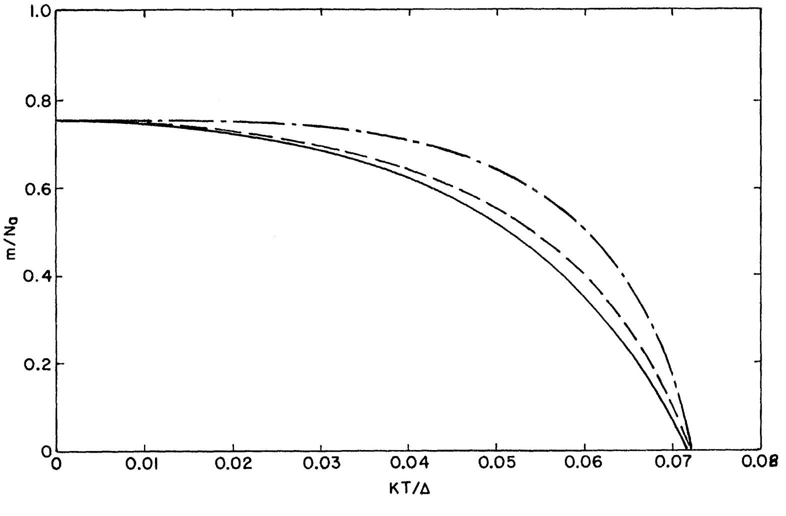

FIG. 3. Magnetization $M/N_a$ vs $KT/\Delta$ using a square density of states for $N_e/N_a=0.75$ is given by the solid lines, the dashed line gives the experimental results of Jarrett *et al.* (Ref. 8) for $Fe_{0.75}Co_{0.25}S_2$, and the dot-dashed line gives the magnetization found from the Weiss molecular field theory.

lomb interaction by negligible intra-atomic exchange (we refer here to exchange without the self-Coulomb interaction included). This model is described by the following Hamiltonian:

$$\mathcal{H}=\sum_{ij\alpha\beta\sigma} h_{ij}\,C^{\dagger}_{i\alpha\sigma}\,C_{j\beta\sigma}\,P_i\,P_j \;. \tag{12}$$

Here, $\alpha$ and $\beta$ label the particular orbital that the electron hops into and $P_i$ is a projection operator which guarantees that the total number of electrons on a site never deviates by more than one electron from the average number of electrons per site. For example, if there is an average of three and a half electrons per site, an electron can jump from a site containing four electrons to a site containing three but not to another site containing four electrons. This guarantees that the very large Coulomb energy always has its minimum value. The effect of the intra-atomic Coulomb interaction is thus replaced by these projection operators. Following our treatment for the single-band model, we consider the motion of either an excess of electrons or deficiency of electrons (i.e., "holes") from atom to atom. We will again find that "ferromagnetic" paths are the most important ones. Whenever such an excess electron or "hole" hops onto a site, in the next hop any one of the electrons (or holes) on the atom is equally likely to hop off. Then, following our approximation, we must multiply the number of possible paths taken by a "hole" or electron by the probability of the net spin of each atom along the path remaining the same, which is the probability of an electron of the same spin always being the one to make each successive hop. This probability for a path of hops is equal to

$$(1-\bar{n}_{-\sigma})^{q}\;, \tag{13}$$

where $\sigma$ is the spin of the electron or "hole" following the path and $\bar{n}_{-\sigma}$ is given by

$$\bar{n}_{-\sigma}=(N_e-\sigma m)/2pN_a\;,$$

where $p$ is the number of orbitals of each spin per site. Then, we simply replace $1-n_{-\sigma_h}$ in Eq. (4a) by $1-\bar{n}_{-\sigma_h}$ to find $Z$, and from $Z$, we find

$$m=N_e\tanh\tfrac{1}{4}\beta\{-(1/2pN_a)\textstyle\sum_{\vec{k}}[f(-\epsilon(\vec{k})(1-\bar{n}_{\downarrow}))$$
$$-f(-\epsilon(\vec{k})(1-\bar{n}_{\uparrow}))]\epsilon(\vec{k})\}\;, \tag{14a}$$

$$\chi=N_e/(KT-K\Theta)\;, \tag{14b}$$

where

$$K\Theta=(1/4p)(N_e/N_a)(1/N_a)\textstyle\sum_{\vec{k}}\epsilon(\vec{k})^2 f'(-\epsilon(\vec{k})(1-\bar{n}_{\downarrow}))\;. \tag{14c}$$

Unfortunately, we find from Eq. (14a) and (14b) that if $p>1$, the saturation magnetization per atom is greater than the magnetic moment per atom calculated from the Curie constant, and such behavior is not observed in any known experimental system to which this strong interaction itinerant model might be applicable. This indicates that the intra-atomic exchange interaction must also be taken large. A multiband version of the treatment given in this paper with intra-atomic exchange taken as very large will reduce in the classical spin (i.e., large spin) limit to de Gennes's treatment of the Zener double-exchange model of ferromagnetism. Such a model of ferromagnetism might be applicable to iron metal which appears to have nearly equal paramagnetic and saturation moments, suggesting a localized spin model,[11] but has a Fermi surface at low temperature and evidence of $d$-electron conductivity,[12] which suggests itinerant $d$ electrons.[12] In order to understand the magnetic properties of iron metal in terms of such a model, however, it is necessary to determine whether such a model would predict the existence of a well-defined Fermi surface in the completely ferromagnetic state and whether the experimental Fermi surface of iron, in particular, is reproduced. More will be said about this in future work.

## III. COMPARISON OF PRESENT MODEL WITH OTHER NARROW-BAND MODELS

We have already mentioned the fact that a multiband version of the model presented in this paper for infinite intra-atomic exchange and Coulomb interactions, but with exchange much larger than Coulomb interaction, is, for infinite atomic spins, de Gennes's treatment of Zener's theory of double exchange.[13] In this case, the probability of hopping from site to site is the average of the cosine of half the angle between neighboring site spins. Since this has its maximum value when the spins are all aligned, the band is narrowed in the paramagnetic state, leading to ferromagnetic ordering at low temperatures. In both models, we obtain a Curie-Weiss susceptibility when the excess carriers in the band form a degenerate gas, and non-Curie-Weiss behavior for higher temperatures or lower concentrations of excess carriers. In both models, the Curie constant yields a magnetic moment which agrees with the saturation moment.

Another comparison which would be constructive is a comparison between Green's function found in the present approximation and that found in Hubbard's approximation[2] and in the work of Harris and Lange.[4] To make this comparison, the one-electron Green's function will be calculated for a half-filled band, and the quasiparticle energies will be found from it and compared with Hubbard's work. The one-electron Green's function can be written as

$$G_{ii,\sigma\sigma}(t)=\langle\langle c_{i\sigma}, c^{\dagger}_{i\sigma}\rangle\rangle=\oint_{c_1} d\omega_1\oint_{c_2} d\omega_2\, e^{i(\omega_2-\omega_1)t}$$
$$\times\sum_{\alpha}\left\langle\alpha\right|e^{-\beta\mathcal{H}}\left(\frac{1}{\omega_2-\mathcal{H}}\,c_{i\sigma}\,\frac{1}{\omega_1-\mathcal{H}}\,,\;c^{\dagger}_{i\sigma}\right)\left|\alpha\right\rangle\;, \tag{15}$$

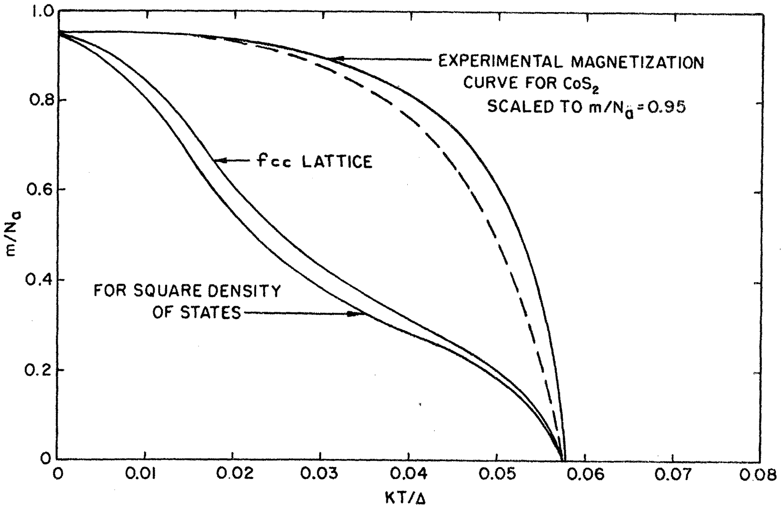

FIG. 4. $M/N_a$ vs $KT/\Delta$ for $N_e/N_a = 0.95$ for both a square density of states and for the density of states for an fcc lattice with near-neighbor tight-binding functions. Dashed line is $M/N_a$ vs $KT/\Delta$ from Weiss molecular field theory of Stoner theory in the large $U/\Delta$ limit. The $M/N_a$-vs-$KT/\Delta$ curve is also shown for pure CoS$_2$ scaled to the magnetization and Curie temperature of the $N_e/N_a = 0.95$ system (Ref. 8).

where $|\alpha\rangle$ is a state with spin $\alpha$ and no "holes" (i.e., an exactly half-filled band). The Hamiltonian is given by

$$\mathcal{H} = \sum_{ij\sigma} h_{ij}(a_{i\sigma}^\dagger a_{j\sigma} + b_{i\sigma}^\dagger b_{j\sigma}) + U \sum_i n_{i\dagger} n_{i\dagger} , \qquad (16)$$

where

$$a_{i\sigma} = (1 - n_{i,-\sigma}) c_{i\sigma} , \quad b_{i\sigma} = n_{i,-\sigma} c_{i\sigma} ,$$

which is the large-$U$ limit of the Hubbard Hamiltonian.[2,4] The contours are chosen such as to enclose all the poles on the real axis (which range from $\omega = U + \Delta$ to $\omega = -\Delta$, where $\Delta$ is half the bandwidth). Using the fact that

$$\mathcal{H}|\alpha\rangle = 0 ,$$

we obtain

$$G_{ii,\sigma\sigma}(t) = \oint_c d\omega_2 \biggl( \bigl|{}_{\text{hole}}\langle i\beta | c_{i\sigma} | \alpha\rangle\bigr|^2 e^{i\omega_2 t} \times {}_{\text{hole}}\left\langle i\beta \left| \frac{1}{\omega_2 - \mathcal{H}} \right| i\beta \right\rangle_{\text{hole}} + \bigl|{}_{\text{electron}}\langle i\beta | c_{i\sigma}^\dagger | \alpha\rangle\bigr|^2 e^{-i\omega_2 t} \times {}_{\text{electron}}\left\langle i\beta \left| \frac{1}{\omega_2 - \mathcal{H}} \right| i\beta \right\rangle_{\text{electron}} \biggr) , \qquad (17)$$

where $|i\beta\rangle_{\text{electron}}$ is state $|\alpha\rangle$ with a spin $\sigma$ electron created at site $i$ and $|i\beta\rangle_{\text{hole}}$ is $|\alpha\rangle$ with a spin $\sigma$ electron anihilated at site $i$. Using the fact that

$$|i\beta\rangle_{\text{hole}} = a_{i\sigma}|\alpha\rangle, \quad |i\beta\rangle_{\text{electron}} = b_{i\sigma}^\dagger|\alpha\rangle ,$$

combined with the anticommutation relations

$$\{c_{i\sigma}^\dagger, a_{i\sigma}\} = 1 - n_{i,-\sigma} , \quad \{c_{i\sigma}, b_{i\sigma}^\dagger\} = n_{i,-\sigma} ,$$

we obtain from Eq. (17)

$$G_{ii,\sigma\sigma}(t) = \int_c d\omega_2 \bigl[ (1 - n_{-\sigma}) e^{i\omega_2 t} \times {}_{\text{hole}}\langle i\beta | (\omega_2 - \mathcal{H})^{-1} | i\beta\rangle_{\text{hole}} + n_{-\sigma} e^{-i\omega_2 t} {}_{\text{electron}}\langle i\beta | (\omega_2 - \mathcal{H})^{-1} | i\beta\rangle_{\text{electron}} \bigr] . \qquad (18)$$

We have assumed that $\langle i\beta | (\omega_2 - \mathcal{H})^{-1} | i\beta\rangle$ is independent of $|i\beta\rangle$, which is true in the ferromagnetic-path approximation. Using this approximation, which was used in Sec. II to find the partition function, to evaluate the resolvent $\langle i\beta | (\omega_2 - \mathcal{H})^{-1} | i\beta\rangle$ and Fourier transforming Eq. (18), we obtain

$$G_{ii,\sigma\sigma}(\omega) = (1 - n_{-\sigma}) \sum_{\vec{k}',\sigma'} \frac{1}{\omega + \epsilon(\vec{k})(1 - n_{-\sigma'})} + n_\sigma \sum_{\vec{k},\sigma'} \frac{1}{\omega - \epsilon(\vec{k}) n_{-\sigma'} - U} . \qquad (19)$$

Like the Green's function in Hubbards first paper[2] on correlations in narrow bands, there are two bands separated by an energy $U$. The spectual weight of each band is the same as that occurring in Hubbard's Green's function, which is required by the sum rules of Harris and Lange.[4] The major difference between this theory and Hubbard's theory is the fact that the Green's function of spin $\sigma$ has poles at both the energies that were assigned to spin-up and to spin-down electrons in Hubbard's paper. This must be the case because if an electron is created on a site already containing an electron of opposite spin, either of the two electrons on that site can move around the lattice as a free particle. A similar result holds for an electron annihilated on a site containing one electron.

Like Hubbard's first paper, this theory does not give quasiparticle lifetime broadening. In his third paper on this problem, Hubbard includes lifetime broadening by a renormalized Green's-function decoupling procedure. The bandwidth in the paramagnetic state found by this procedure is in the infinite-$U$ limit equal to the ferromagnetic state bandwidth. This would imply that there is no ferromagnetic ordering. We know, however, from the arguments given in Sec. II, that this bandwidth is excessive for the paramagnetic state. The width of the major part of the band must be narrower in the paramagnetic state, aside from band tails containing very few states, because there are fewer possible paths on which the holes may hop, appearing in the expansion of the partition function or resolvent.

## IV. APPLICATION TO IRON-COBALT DISULPHIDE MIXTURES

The plot of $T_c$ vs electron concentration (Fig. 2) for $Fe_{1-x}Co_xS_2$ ($x$ goes from 0 to 1 where $x=N_e/N_a$) appears to agree with that found from our model qualitatively except near $x=0$ when it is not expected to be valid, and at $x$ near 1. In I, it was argued that for $x$ near 1, the theory could give the wrong $T_c$ because for $U$ large but not infinite, there will be a Heisenberg-model-like effective ferromagnetic exchange coupling in a two-band generalization of the Hubbard model, which keeps $T_c$ from falling to 0 at $x=1$ as it does in our model. The situation is not that simple, however, because not only does the magnetization-vs-temperature curve found from our model not agree with the experimental system, but the conductivity of pure $CoS_2$, which should on the basis of our model be zero because in this limit there is one electron per site and the large $U$ keeps electrons from hopping onto the same site, is actually metallic. As was remarked in I, it appears that there is an effective increase in $h_{ij}$ as we move from $x=0$ to $x=1$, and near $x=1$, we no longer have $U$ greater than the bandwidth. A possible reason for this will now be given.

First of all, we rule out the possibility that the cobalt atoms form separate impurity bands. If this were the case, either the conductivity would be zero because the large $U$ would keep the electrons from hopping (there is exactly one electron per impurity band atom), or the saturation magnetization would have to fall below the number of electrons in the system for the conductivity to be nonzero and this is not observed for $x<0.95$. The saturation magnetization does, however, fall below its maximum possible value for $x$ greater than 0.95 implying obviously that there is polar state admixture at this point. Imagine that instead of forming impurity bands, the cobalt atoms formed resonant states near the bottom of the conduction bands. We could equally well think of the Fe ions forming resonant "hole" states near the bottom of the "hole" bands. In order for the "holes" in these states to conduct, they must hop onto cobalt ions. The level width of the resonant state should be a measure of this effective hopping integral if the iron atoms are, on the average, more than a near-neighbor distance apart. Since the density of states near the bottom of the band is usually smaller than average these level widths and hence the effective $h_{ij}$ will be reduced below that of pure $CoS_2$. We postulate then that near $x=1$, the effective hopping is such that $h_{ij}/U$ is great enough to allow polar state admixture. For lower $x$, however, the effective $h_{ij}/U$ is much smaller, and thus the theory of this paper should be more appropriate. In this picture, then, pure $CoS_2$ should be described by ordinary Stoner theory, but for values of $x$ less than about 0.95, the theory of this paper should be more appropriate.

Throughout I and Sec. II of this paper, we treat the exclusion of holes from nonferromagnetic paths probabilistically, which leads to hole eigenstates labeled by wave vector $\vec{k}$. This can easily be shown to be rigorously true when the spins are randomly distributed and when the magnetization is fairly high, or for all magnetization when the range of $h_{ij}$ is large. In all other cases, however, the effect of the lifetime broadening of the quasiparticle states is to smooth out the details of the density of states. By the arguments given in Sec. II A, however, this will not change the result that the model is ferromagnetic for between a nearly full and a half-filled band.

Another point to remember is that the cobalt-iron disulphide system is a disordered system even in the ferromagnetic state. Thus, there should be rounding out of the density of states even in the magnetically ordered state. The presence of additional spin-disorder scattering will probably not change the shape of the density of states significantly except to introduce the narrowing effect. The presence of disorder in both ferromagnetic and paramagnetic states makes possible an interesting optical-absorption experiment. Because of the disorder it may be possible to observe the density of states directly by looking at intraband absorption. This should make it possible to observe changes in the density of states predicted when the system orders magnetically.

## V. CONCLUSION

The single $s$-band Hubbard-model electronic system was shown to be ferromagnetic in the infinite interaction limit over a wide range of electron density. An approximate calculation was then made of the magnetization, Curie temperature, and susceptibility. The results were used to explain experimental data on transition-metal disulphides. In order to understand the magnetic properties of these compounds, it was necessary to give a short discussion of disordered systems, which will be discussed in more detail in future publications. The results of calculations were then compared to other theories of narrow-band systems.

The main result of these calculations is that for strongly interacting electrons, it is possible to have ferromagnetism caused by a change in the bandwidth when the system orders rather than a band splitting, which is obtained in the more conventional Hartree-

Fock itinerant electron theory of magnetism.

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# Interaction Effects between Nearly Magnetic Cobalt Impurities in Gold

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The magnetization of *Au*-Co alloys was studied over a large range of concentrations ($0.05 < c < 4$-at.% Co), fields ($0 < H < 70$ kOe), and temperatures ($0.05\ \mathrm{K} < T < 200$ K). Magnetization and specific-heat results are well represented by a model with the following characteristics: (a) The isolated Co atoms are not magnetic. (b) The isolated pairs are also not magnetic, but have a Kondo temperature nine times smaller than that of isolated Co atoms. (c) The groups of three or more atoms are magnetic and lead to magnetic ordering at very low temperatures.

## I. INTRODUCTION

### A. General Survey

Blandin and Friedel[1] have classified the behavior of the transition-metal atoms in noble metals into two types. For the first type, the Stoner condition[2] for magnetism, $U_{\mathrm{eff}}\,\rho_d(E_F) > 1$, is verified; here $\rho_d(E_F)$ is the $d$ density of states, and $U_{\mathrm{eff}}$ the effective intra-atomic interaction in the Anderson Hamiltonian.[3] Thus Cr, Mn, and Fe atoms in Cu and Au hosts carry a magnetic moment. For the second type, the previous condition is not satisfied; thus V, Ti, and Ni atoms in the same hosts are not magnetic. The Co impurity in Cu and Au is between the two kinds of behavior, just at the limit of magnetism.

In the theories of the Kondo effect, it is assumed that the condition for magnetism is satisfied.[4–9] The localized spin $S$ interacts with the conduction electrons, via an antiferromagnetic interaction. This $s$-$d$ interaction, $-2J\vec{S}\cdot\vec{s}$, leads, in the second Born approximation, to a logarithmic divergence in the scattering cross section as the temperature decreases.[4] This explains the resistivity minimum.[10] More sophisticated techniques[8] are necessary to remove this divergence at low temperatures: A new many-body state builds up below the Kondo temperature $T_K$; this quasibound state is usually represented by a negative polarization of the electrons around the impurity, leading to a compensation of the local magnetic moment. The relevance of this problem was increased by the experimental work of Daybell and Steyert on the *Cu*-Fe system,[11] and by the suggestion of Schrieffer[5]