Theory of Magnetic Properties of Narrow-Band Solids

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Magnetic properties of narrow-band solids are considered by calculating the spontaneous magnetization and susceptibility as a function of temperature of the Hubbard Hamiltonian, which should be applicable to them, in the limit as the ratio of interaction to hopping energy approaches infinity. Results are found for those lattices shown rigorously by Nagaoka to have a ferromagnetic ground state. The calculation is performed by a diagrammatic expansion of the partition function in which the choice of diagrams to be summed dominates the expansion in the limit of temperatures much less than the hopping energy. The model is expected to be applicable to the transition-metal disulfides $Fe_{1-x}Co_xS_2$ and $Co_{1-x}Ni_xS_2$ $(0<x<1)$, and the results of this paper are compared with experiments done on these compounds.

I. INTRODUCTION

Jarrett *et al.*[1] have observed that the compounds $Fe_{1-x}Co_xS_2$ (x goes from 0 to 1) appear to have metallic electrical conductivity and at the same time magnetic properties of a ferromagnetic localized spin system. That is, these compounds are ferromagnetic, they obey a Curie-Weiss law for temperatures above their Curie temperature, and the saturation moment agrees with the moment calculated from the measured Curie constant. Furthermore, the saturation moment is just

$$(1-x)S_{\mathrm{Fe}}+xS_{\mathrm{Co}} \text{ for } Fe_{1-x}Co_xS_2$$

and

$$(1-x)S_{\mathrm{Co}}+xS_{\mathrm{Ni}} \text{ for } Co_{1-x}Ni_xS_2 \quad ,$$

for most x between 0 and 1, where S_{Fe}, etc., represent the free-atom magnetic moments for the respective atoms in the appropriate crystal field for these compounds. Evidence is presented in Ref. 1 that there are two narrow partially filled bands (bandwidth ~1 eV or less) which are responsible for both the electrical conduction and magnetic properties.

It was shown,[2] using the exact results of Lieb and Wu,[3] that a near-neighbor hopping Hubbard model in one dimension exhibits localized spin behavior for interaction energy infinitely greater than hopping energy even for a less than half-filled band (which exhibits metallic conductivity). In this paper, the temperature and field dependence of the magnetization of the three-dimensional Hubbard model with infinite interaction is investigated. It can be shown using a canonical transformation[4] that the Hubbard Hamiltonian

$$\mathcal{H}=\sum_{ij}h_{ij}C^{\dagger}_{i\sigma}C_{j\sigma}+U\sum_i n_{i\uparrow}n_{i\downarrow} \tag{1}$$

in the infinite-U limit reduces to

$$\mathcal{H}_{\mathrm{eff}}=\sum_{ij}h_{ij}a^{\dagger}_{i\sigma}a_{j\sigma} \, . \tag{2}$$

Here, $C_{j\sigma}$ is the annihilation operator for an electron of spin σ in the Wannier function on site j, U is the interaction energy, h_{ij} is the hopping matrix element,

$$\text{and} \quad \begin{aligned} n_{i\sigma}&=C^{\dagger}_{i\sigma}C_{i\sigma} \\ a_{i\sigma}&=(1-n_{i,-\sigma})C_{i\sigma} \, . \end{aligned} \tag{3}$$

Equation (2) only allows electrons to hop onto a site not occupied by another electron of either spin. Nagaoka[5] has shown rigorously that the system described by Eq. (2), restricted to near-neighbor hopping, has a ferromagnetic ground state if it contains one electron less than the number of sites, for simple-cubic and body-centered-cubic lattices, and for hexagonal closed-packed and face-centered cubic lattices for h, the near-neighbor hopping matrix element, greater than zero. In this paper the magnetization and susceptibility of this system will be calculated as a function of electron density and temperature.

We proceed by evaluating the partition function as follows:

$$Z=\mathrm{Tr}e^{-\beta\mathcal{H}_{\mathrm{eff}}}=\sum_{\{i\},\,\alpha\{i\}}\langle\{i\},\,\alpha\{i\}|e^{-\beta\mathcal{H}_{\mathrm{eff}}}|\{i\},\,\alpha\{i\}\rangle \, , \tag{4}$$

where $|\{i\},\,\alpha\{i\}\rangle$ denotes a Slater determinant of N_e Wannier functions (N_e is the number of electrons), $\{i\}$ denotes the locations of "holes" (i.e., sites not occupied by an electron of either spin), $\alpha\{i\}$ represents the set of spins of all electrons on sites not belonging to $\{i\}$, and $\mathcal{H}_{\mathrm{eff}}$ is given by Eq. (2). If the exponential is expanded in a Taylor series in powers of β, Eq. (4) reduces to

$$Z=\sum_{\{i\}\alpha\{i\}}\sum_n A_n(\{i\},\,\alpha\{i\})\frac{1}{n!}(\beta h)^n \tag{5}$$

for near-neighbor hopping. $A_n(\{i\},\,\alpha\{i\})$ is the number of paths of the N_a-N_e holes, where N_a is the

number of lattice sites, which together involve n near-neighbor hops which either take each "hole" around in a closed path ending on the site on which it began or interchange positions of two or more holes. (A is negative for the "exchange" paths.) At the same time the paths must return the electron spins to the configuration denoted by $\alpha\{i\}$. All terms in Eq. (5) will be found to be positive if "hole" densities are small, because for simple-cubic and body-centered-cubic lattices only even n contribute; for the other lattices considered by Nagaoka there are also only positive terms if h is taken > 0. Since we will be considering the regime in which $KT \ll h$, we will see that high orders (i.e., large paths) will tend to dominate Eq. (5).

In Sec. II, we will evaluate the partition function in this way for the trivial case of a spinless free-fermion system, i.e., Eq. (1) without spin and without the interaction term. Since this problem has an exact solution, we can use it to test the method. We may then apply what we learn about the physical significance of the various paths that contribute in this problem to the more interesting problem of finding the magnetization predicted by Eq. (2) with spin. This problem, the contribution of this paper, is solved in Sec. III. In Sec. IV, these results are compared with experiment.

II. SPINLESS FERMION PROBLEM

Let us first consider the spinless problem for a nearly filled or nearly empty band. Here, we will not restrict h_{ij} to near neighbors but will consider the general case. For this problem, Eq. (4) becomes

$$Z = \sum_{\{l\}} \sum_{n} \langle \{l\} | \frac{1}{n!} (-\beta)^n (\sum_{ij} h_{ij} C_i^\dagger C_j)^n | \{l\} \rangle , \qquad (6)$$

where the number of electrons (or holes) located at the sites $\{l\}$ is taken to be much smaller than the number of sites in the lattice. Then, since for most terms in the summation over $\{l\}$, the electrons (or holes) are always quite far apart, the nth order term in Eq. (6) consists predominantly of closed paths in which each electron (or hole) is taken from its site and returned in the end to its original site. The numbers of sites in the paths of the various electrons (or holes) will be denoted by $\{n_p\} = n_1, n_2, \ldots, n_{N_e}$. Using the fact that the number of ways of distributing n hops of the electron (or hole) among the set $\{n_p\}$ is

$$n!/n_1!, \ldots, n_{N_e}!$$

and writing h_{ij} as

$$h_{ij} = (N_a)^{-1} \sum_{\vec{k}} \epsilon(\vec{k}) e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)} ,$$

the nth order term of Eq. (6) is found to be

$$Z = \prod_{p=1}^{N_e} \sum_{n_p} \left(-\frac{\beta}{N_a} \right)^{n_p} \frac{1}{n_p!} \prod_{l_p=1}^{n_p} \epsilon(\vec{k}_{p,l_p}) \times \sum_{\vec{R}_{p,l_p}} \exp i\vec{k}_{p,l_p} \cdot (\vec{R}_{p,l_p} - \vec{R}_{p,l_p+1}) , \qquad (7)$$

where N_e is the number of electrons (or holes), $\vec{R}_{p,n_p+1} = \vec{R}_{p,1}$ for all p, and $\vec{k}_{p,l_p}$ is k associated with the l_pth hop of the pth electron (or hole). Then, on summing over the R's, Eq. (7) becomes

$$Z = \prod_{p=1}^{N_e} \sum_{\vec{k}_p n_p} (-\beta)^{n_p} \frac{1}{n_p!} \epsilon(\vec{k}_p)^{n_p}$$

$$= \sum_{\vec{k}_1, \vec{k}_2, \cdots, \vec{k}_{N_e}} \exp[-\beta \sum_{p=1}^{N_e} \epsilon(\vec{k}_p)] . \qquad (8)$$

This is the partition function for a noninteracting spinless system if the Pauli-exclusion principle is neglected. Equation (8) is a valid approximation if the mean number of lattice sites between electrons (or holes), which is of the order of $(N_a/N_e)^{1/3}$, is much greater than unity.

As the electrons (or holes) become more concentrated, their paths can no longer be considered to be noncrossing. We then must also consider paths in which different electrons (or holes) exchange places. Collision paths (i.e., paths in which two particles arrive simultaneously on the same site) are included, because by including exchange graphs, the anticommuting property of the C operators automatically cancels the contribution from such graphs. The contribution due to such exchange paths, which must be added to Eq. (7), looks like Eq. (7) multiplied by -1, with the restriction on the summation over $\{\vec{R}_{p,n_p}\}$ changed as follows:

$$\vec{R}_{p,n_p+1} = \vec{R}_{p',1} ,$$

$$\vec{R}_{p',n_{p'}+1} = \vec{R}_{p'',1} ,$$

where $p' \neq p$ and $p'' \neq p'$. When summed over the R's, we get the negative of all those terms in Eq. (8) with two or more $\vec{k}$'s equal. When this contribution is added to Eq. (8), it cancels all terms in Eq. (8) with two or more equal k's leaving

$$Z = \sum_{\vec{k}_1 \neq \vec{k}_2, \ldots, \vec{k}_{N_e}} \exp[-\beta \sum_{p=1}^{N_e} \epsilon(\vec{k}_p)] , \qquad (9)$$

the well-known partition function for a noninteracting spinless Fermi system.

III. NARROW-BAND SYSTEM WITH SPIN

The first step in the calculation of the partition function using the effective Hamiltonian of Eq. (2) is the enumeration of the various hole paths which contribute to order n in Eq. (5).

All possible paths connecting near-neighbor sites in a three-dimensional lattice and returning to the origin can be constructed out of two types, which we will call a "loop" and a "line." A loop consists of any closed path which returns to its start-

ing point. A line is a path which starts at some point in the lattice, ends at any point, and which must be traversed once in each direction by a hole. A line may connect loops to produce reducible graphs in the language of Abrikosov, Gor'kov, and Dzyaloshinski.[6] In most cases, a loop will be a low-symmetry loop, using the language of Ref. 2. Spins are randomly distributed on such a loop. This means, for example, that if a loop is simple (does not cross itself), a hole must move around the loop as many times as there are electrons on the loop in order to return the spins to their original configuration, since each time around the loop the hole cyclically permutes the loop's electron spins by one lattice site. It was shown in Ref. 3, however, that there are also high-symmetry loops for which the hole need not travel as many times around the loop as there are electrons to return the spins to their original configuration. These loops have the electron spins on them ordered in such a way that when they are cyclically permuted a fraction of the way around the loop, the loop has returned to its original spin configuration. The order n to which a particular path contributes is equal to the number of hops of the hole around the path necessary to return the electrons on that path to their original spin configuration.

Let us now determine which type of path gives the largest nth order contribution to Z in Eq. (5). It has already been mentioned that for $KT \ll h$, terms with $n \gg 1$ dominate in Eq. (5). By definition, a line of p sites always contributes $2p$ hops to n. A simple low-symmetry loop of p sites contributes $p(p-1) \approx p^2$ hops. A self-crossing low-symmetry loop of p sites must be traversed at least $p(p-1)$ times and there will be restrictions on how it may be traversed, thus reducing the number of such paths. A ferromagnetic loop (i.e., a loop having electrons of the same spin on all its sites) is the highest-symmetry loop and always contributes an order p. The number of lines of p sites is equal to the number of near-neighbor hopping paths of p sites, which is z^p, where z is the coordination number of the lattice. The total number of loops of p sites is, on the basis of random walk theory, $\sim z^p/p^{3/2}$.[7] For a given order n, a low-symmetry loop will give a smaller contribution than a high-symmetry loop. The reason for this is that a given contribution n_1 to the number of hops from a high-symmetry loop comes from a loop with more sites than a corresponding low-symmetry loop giving the same contribution n_1. Since we have seen that the number of loops with p sites increases with p for large p, we will find that there are many more high-symmetry loops contributing a given n_1 hops than low-symmetry loops, for large n_1.

In general, the number of loops of a particular symmetry, which can be drawn, depends on the total spin of the state being considered in the summation in Eq. (5). It will now be shown that ferromagnetic loops dominate over all loops in Eq. (5) for $n_1 \gg 1$.

For M spin-up electrons and a total of N_e electrons, the total number of ferromagnetic paths of order n, assuming random distribution of spins, is

$$\sim (N_e/N_a)^n[(M/N_e)^n + (1 - M/N_e)^n]z^n/n^{3/2} \quad \text{for } n \gg 1. \tag{10}$$

The bracketed quantity is the probability of making n hops onto sites of the same spin. Equation (10) gives a minimum contribution of $2(\frac{1}{2}z)^n n^{-3/2}$ for $M/N_e = \frac{1}{2}$. The high-symmetry loops can be labeled by an integer q, which is the number of electrons in a unit cell which repeats itself on the loop. Therefore, q is the number of times the loop must be traversed. For a ferromagnetic loop, $q = 1$. The case $q = 2$ is the antiferromagnetic loop, etc. The total number of loops lf lower than ferromagnetic symmetry give a contribution of less than

$$\sum_{q=2}^{n^{1/2}} z^{n/q}(q/n)^{3/2} < n^{1/2} z^{n/2}(2/n)^{3/2}, \tag{11}$$

where q is the number of times the path must be traversed to return to its original configuration. (Of course, this summation is restricted to q such that n/q is an integer.) This contribution is much less than the number of ferromagnetic loops given in Eq. (10) for $n \gg 1$. [Single lines are included in Eq. (11) as $q = 2$ loops.]

Next, we must consider multiply-self-crossing loops. A graph of the type illustrated in Fig. 1 will not contribute, in general, unless it is ferromagnetic. The reason for this is that it contains loops which cross themselves more than once, and since such crossings reorder the spins on the loop for every trip of the hole around the loop, it will be impossible for the hole to return the spins to their original configuration in any finite number of times around the loop (for $n \gg 1$). The only multiply-crossing loops which do contribute are of the form illustrated in Fig. 2. This loop has several distinct noncrossing loops. Motion of the hole around the path does not reorder the spins on any loop or transfer spins from one loop to another. Thus, each loop may be traversed by the hole as many times as necessary to cyclically permute the spins on it back to their original configuration without interfering with any other loop. Some of the

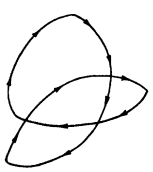

FIG. 1. This is a multiply-crossing "hole" path. The arrows denote the direction in which it is traversed.

loops on such a path may be ferromagnetic and others not. If of n hops taken up by this path, n' hops belong to nonferromagnetic loops, and the remainder belong to ferromagnetic loops, the total number of such paths is found to be less than

$$\sum_{n'} \binom{n}{n'} \left[\left(\frac{2}{n'}\right)^{3/2} z^{n'/2}\right]\left[\left(\frac{1}{n-n'}\right)^{3/2} z^{(n-n')}\right]$$

$$\leq 2^n \left(\frac{4}{n}\right)^{3/2}\left(\frac{2}{n}\right)^{3/2} z^{3n/4} \qquad (12)$$

for large n. Here

$$(2/n')^{3/2} z^{n'/2}$$

is the total number of loops containing $n'/2$ sites. The contribution of low-symmetry loops contributing the n' sites is clearly less than this number. Then, for large n, Eq. (10) is clearly much greater than the sum of Eqs. (11) and (12), and hence, ferromagnetic loops dominate over all other loops. There could, however, be significant contributions from the paths considered in Ref. 8, which consist of several lines which have one end passing through the origin. The magnetic ordering, however, is due mainly to the ferromagnetic loops. The contributions from the ferromagnetic loops and the paths considered in Ref. 8 to the band edge should be nearly equal for the face-centered cubic lattice for random spin ordering. If we include further than near-neighbor hopping (this is like increasing the effective number of near neighbors), the ferromagnetic paths will at some point always tend to dominate. Hence, we will only include the contribution to ferromagnetic paths.

Let us now evaluate the partition function from Eq. (5), including only ferromagnetic paths. (The same arguments apply to exchange paths.) Following the development in Sec. II for the spinless case, we obtain Eq. (7), with the exchange path contribution subtracted from it, except that $\vec{R}_{p,l_p}$ is now only summed over sites having the same spin. For each hole we get two contributions, one for summing over spin-up sites only and one for spin-down sites. Their respective contributions depend on the total magnetization of the system. The result must then be averaged over all possible locations of spin-up and spin-down electrons and initial locations of holes. If N_h/N_a is not so small that all holes lie in the band tail, [8] we neglect the contribution from highly improbable distributions of electron spins, in which large numbers of electrons of the same spin lie close to each other. Thus, we assume up- and down-spin electrons to be randomly distributed and make a random-phase assumption by replacing the summation

$$\sum_{\vec{R}_{p,l_p}} \exp[i(\vec{k}_{p,l_p-1} - \vec{k}_{p_1,l_p})\cdot \vec{R}_{p,l_p}] \qquad (13)$$

either with M if we are summing $\vec{R}_{p,l_p}$ over spin-up sites, or with $N_e - M$ if we are summing it over spin-down sites multiplied by the Kronecker delta $\delta(\vec{k}_{p,l_p=1}, \vec{k}_{p,l_p})$. Performing these operations, the partition function is found to be

$$Z = \sum_{N_{h\uparrow}=0}^{N_h} \sum_{\substack{\vec{k}_1\neq\vec{k}_2\neq\cdots\vec{k}_{N_{h\uparrow}} \\ \vec{k}_{N_{h\uparrow}+1}\neq\vec{k}_{N_{h\uparrow}+2}\neq\cdots\vec{k}_{N_h}}} \times \exp\left[\beta\sum_l \epsilon(\vec{k}_l)\left(\frac{N_{\sigma l}}{N_a}\right)\right]\left(\frac{N_e}{M}\right), \qquad (14)$$

where $N_\uparrow = M$ and $N_\downarrow = N_e - M$, and where $N_{h\uparrow}$ is the number of holes taking spin-up paths.

It will be more convenient in the discussion that follows to use the grand canonical partition function defined as follows:

$$Q = \sum_{N_h} e^{\beta u N_h} Z_{N_h} \cong \prod_{\vec{k}\sigma} (1 + e^{\beta[\epsilon(\vec{k})(N_\sigma/N_a) - u]})\binom{N_e}{M}, \qquad (15)$$

where u is the chemical potential of the holes. From Eq. (15) we find

$$N_h = \frac{1}{\beta}\frac{\partial}{\partial u}\ln Q = \frac{1}{N_a}\sum_{\vec{k}\sigma}\{1 + e^{\beta[\epsilon(\vec{k})(N_\sigma/N_a) - u]}\}^{-1}, \qquad (16)$$

and

$$-\beta H = \frac{\partial}{\partial m}\ln Q = -\ln\frac{M}{N_e - M} - \frac{1}{2N_a}\sum_{\vec{k}}\left[f\left(-\epsilon(\vec{k})\frac{M}{N_a}\right) - f\left(-\epsilon(\vec{k})\frac{N_e - M}{N_a}\right)\right]\beta\epsilon(\vec{k}), \qquad (17)$$

where H is an applied magnetic field, $m = 2M - N_e$, the magnetization, and where

$$f(x) = [e^{\beta(x-u)} + 1]^{-1}.$$

Below the Curie temperature, Eq. (17) becomes for $H = 0$,

$$m = -N_e \tanh\left\{\frac{1}{4}\frac{1}{N_a}\sum_{\vec{k}}\left[f\left(-\epsilon(\vec{k})\frac{M}{N_a}\right) - f\left(-\epsilon(\vec{k})\frac{N_e - M}{N_a}\right)\right]\beta\epsilon(\vec{k})\right\}. \qquad (18)$$

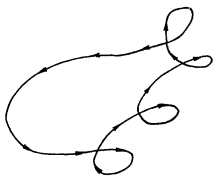

FIG. 2. This is a multiloop path in which each loop does not intersect itself. Again, the arrows indicate the direction traversed by the "hole".

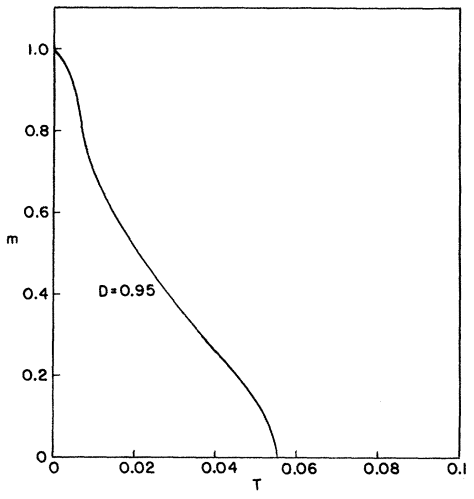

FIG. 3. Spontaneous magnetization m per site plotted against T. m is dimensionless, and T is in units Δ/K. $D=N_e/N_a$.

The solution of this equation gives the spontaneous magnetization. It is easy to see from Eq. (18) that the system will order at sufficiently low temperatures reaching a saturation magnetization of N_e as T approaches zero. Above T_c, we find by linearizing the right-hand side of Eq. (17) in the magnetization that

$$m = N_e H/(KT - K\theta) , \tag{19a}$$

where

$$K\theta = \frac{1}{4}\frac{N_e}{N_a}\ \frac{1}{N_a}\sum_{\vec{k}} \epsilon(\vec{k})^2 f'\left(\tfrac{1}{2}\epsilon(\vec{k})\frac{N_e}{N_a}\right) , \tag{19b}$$

where

$$f'(x) = -\beta[e^{\beta(x-u)}/(e^{\beta(x-u)}+1)^2] .$$

For sufficiently high hole densities, $K\theta$ given by Eq. (19b) becomes a constant and is given by

$$K\theta = \tfrac{1}{4}(N_e/N_a)\epsilon_F^2\rho(\epsilon_F) , \tag{20}$$

where $\rho(\epsilon_F)$ is the density of states for the noninteracting system, and $\frac{1}{2}(N_e/N_a)\epsilon_F = u$. Hence, for sufficiently high hole densities, the spin susceptibility system obeys a Curie-Weiss law above the Curie temperature, and at low temperatures the system orders ferromagnetically, with all spins aligned at zero temperature.

Although the justification for taking ferromagnetic paths was based on an argument assuming near-neighbor hopping only, the argument should hold for a longer range hopping integral, too. Extending the range of the hopping integral is like increasing the effective number of near neighbors. Let us now evaluate the susceptibility, Curie temperature, and magnetization as a function of temperature for a simple model of the electronic structure in which $\rho(\epsilon)$ is taken to be given by

$$\rho(\epsilon) = 1/2\Delta \quad \text{for} \quad -\Delta \le \epsilon \le \Delta$$

and zero otherwise, where Δ is half the bandwidth. The spontaneous magnetization as a function of temperature, the Curie temperature as a function of density, and $K\theta$ as a function of temperature and density have been obtained by solving numerically Eqs. (18) and (19b) simultaneously with Eq. (16). The results are shown in Figs. 3–6. The magnetization is found to fall off from its saturation value quite sharply at first, and then fall much more gradually to zero at the Curie temperature, as seen in Fig. 3. Similar results were found for

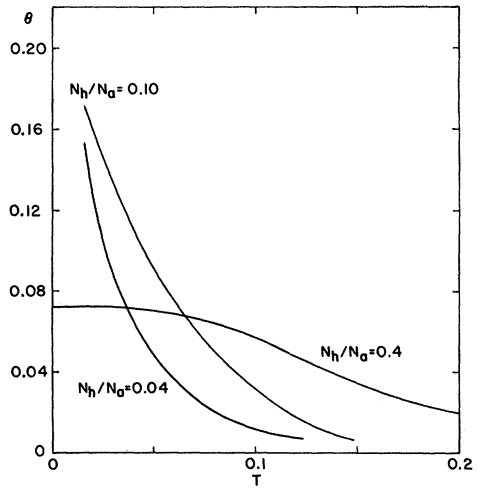

FIG. 4. θ against T, both in units of Δ/K.

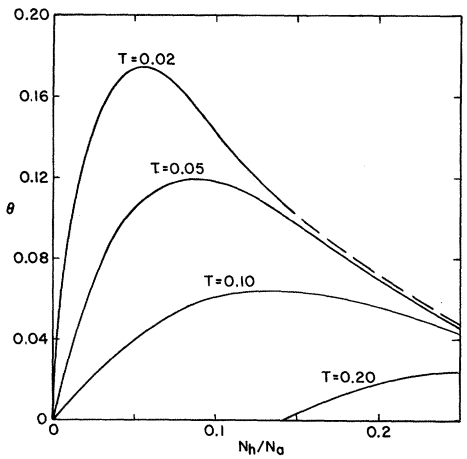

FIG. 5. θ versus N_h/N_a; θ in units of Δ/K.

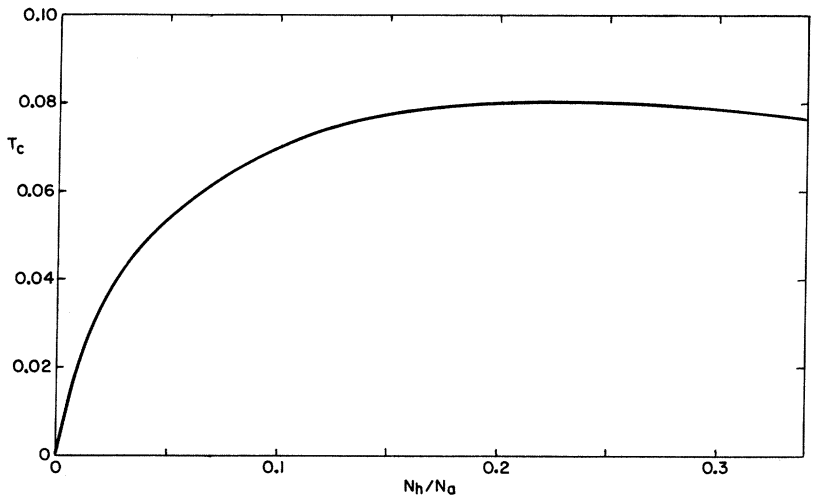

FIG. 6. T_c versus N_h/N_a; T_c in units of Δ/K.

hole densities other than the one illustrated in Fig. 3. From the behavior of $K\theta$ in Fig. 4, we see that the system does not have a Curie-Weiss susceptibility at low hole densities, i.e., for densities to the left of the peak in the T_C versus N_h/N_a curve.

The method described in this paper is probably only accurate in the fairly low-hole-density regime. As the hole density increases, the Curie temperature reaches values at which the ferromagnetic paths should no longer dominate. Also, at higher hole densities, since the exchange contribution is large, paths other than ferromagnetic paths become more important. At still higher hold densities, the approximation breaks down because there are so few sites available for a hole to hop onto that it no longer makes sense to speak of holes hopping.

The physical description of the magnetic ordering in this model appears to be that magnetic ordering occurs because the hold band is narrower in the paramagnetic state than in the ferromagnetic state. Thus, the holes have lower energy in the ferromagnetic state.

IV. COMPARISON OF THEORY WITH EXPERIMENTS ON TRANSITION-METAL DISULFIDES

Transition-metal disulfides are actually believed to be described by a two-band model. Consider the following two-band Hamiltonian in which only intra-atomic Coulomb and exchange integrals are included:

$$\mathcal{H} = \sum_{\substack{ij \\ \alpha\beta\sigma}} h_{ij} C^{\dagger}_{i\alpha\sigma} C_{j\beta\sigma} + U \sum_{i\alpha} \left(n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \sum_{\substack{\sigma\sigma' \\ \alpha\neq\beta}} n_{i\alpha\sigma} n_{i\beta\sigma'} \right)$$

$$- J \sum_{\substack{\sigma\sigma' \\ \alpha\neq\beta}} C^{\dagger}_{i\alpha\sigma} C_{i\alpha\sigma'} C^{\dagger}_{i\beta\sigma'} C_{i\beta\sigma} , \qquad (21)$$

where U and J are the intra-atomic Coulomb and exchange integrals, respectively, and α and β label the orbital (there are two relevant orbitals per site corresponding to the two e_g orbitals of the metallic ion). If we assume that the number of electrons is less than the number of lattice sites and U is much greater than h_{ij}, the Hamiltonian describes a system in which electrons hop between sites which can only contain either 0 or 1 electron, as in the one-band model. The difference is that for this Hamiltonian if U and J are taken to be large but not infinite and $U \gg J$, there will be an effective ferromagnetic-exchange interaction due to admixture of states containing two electrons on a site. By contrast, in the one-band model in the large U limit, there is an effective antiferromagnetic exchange.

According to this model, the system should be a ferromagnetic insulator when there is exactly one electron per site. (This should correspond to CoS_2.). However, CoS_2 is observed to be a ferromagnetic metal. A reasonable explanation of this is that in the compound $Fe_{1-x}Co_xS_2$ as x goes from 0 to 1 (i.e., as the number of electrons per metallic site goes from 0 to 1), the ratio h/U increases, and somewhere near $x = 0.95$, h becomes comparable to U and the theory discussed in this paper no longer applies.[9] It is precisely at $x = 0.95$ that the saturation magnetic moment decreases below the number of electrons (its maximum possible value). For $x > 0.95$, the compounds are probably better described by the conventional band theory of magnetism based on the Hartree-Fock approximation. Near $x = 0.95$, apparently, there is a good deal of "polar state" admixture as occurs in a compound undergoing a metal-to-insulator transition. The difference here is that there is less than one electron per site in the conducting band, making the compounds metallic on both sides of this transition a point.

A point of agreement between theory and experi-

ment is that the T_C versus hole concentration curve (Fig. 6) predicted by the theory peaks at $N_h/N_a \approx 0.25$, which corresponds to $x = 0.75$. This is close to the point at which the experimental curve peaks. Although we do not expect the ferromagnetic paths to still dominate at temperatures near the peak in this curve, we still expect the results to be at least semiquantitatively correct. A point of disagreement between theory and experiment is the non-Curie-Weiss behavior of the magnetic susceptibility above T_C predicted by the theory for small hole concentrations, which is not observed in the experiments. For low hole densities, however, the effective ferromagnetic exchange due to virtual admixture of states containing two electron atoms might actually dominate. Since this effective exchange can be described by a Heisenberg model, it should give rise to a Curie-Weiss susceptibility.

Polaron hopping theory is ruled out as a description of these compounds because polaron theory predicts polaron band conductivity decreasing with increasing temperature below a certain temperature and thermally activated hopping above this temperature. The conductivity is observed to decrease steadily with increasing temperature. There could still be some polaron effects, however. It is also possible that rigid-band theory may not describe these mixtures of compounds and that, instead, impurity bands are formed. This is ruled out because if there were cobalt impurity bands, they would have to contain one electron per site in the band. Thus, if their bandwidths were not above a critical value (bandwidth $> U$), they would not conduct electricity. Above this critical value they should be described by conventional band theory of magnetism, which does not predict the localized electron magnetic properties found for these compounds.

Thus, we have seen that it is possible for narrow-band itinerant-electron theory to account for both metallic conductivity and magnetic properties characteristic of localized electrons, exhibited by the same conduction electrons, in a simple experimental itinerant-electron magnetic system.

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