Itinerant Theory of Ferromagnetism and Hund's-Rule Coupling*

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(Received 27 May 1971)

We propose a Zener-like model for narrow bands, which includes the intra-atomic Hund's-rule coupling of d electrons. Each of Hubbard's split bands is then shown to split again into spin-polarized sub-bands, yielding ferromagnetism when the density of Zener electrons is low but yielding antiferromegnetism when the density increases.

In the Hubbard theory of narrow bands,[1] the intra-atomic repulsive interaction is responsible for the insulating properties of materials with partly filled d bands and may also be the cause of antiferromagnetism.[2] However, it is generally considered that the exact ground state of the Hubbard Hamiltonian can never be ferromagnetic. In fact, the Lieb-Mattis theory[3] is inclined to suggest the impossibility of ferromagnetism for a lattice of atoms in orbitally nondegenerate states.

According to Herring,[4] the model which was originally proposed by Zener[5] for mixed-valence oxides, and which exhibits ferromagnetism, might be applicable to explain ferromagnetism in transition metals. This is a lattice of well-separated atoms, identical except that some have x d electrons and others $x+1$, where $1 \leq x \leq 4$. For more than half-filled d shells where $5 \leq x \leq 8$, exactly the same treatment can be extended by substituting "holes" for "electrons," so that the model is valid for cases with more than one d electron (or d hole) per atom. It is further assumed that x electrons at each atomic site are coupled according to Hund's rule to yield the spin of maximum multiplicity, S. If an additional electron, called a Zener electron, appears at an atomic site R, then the electron spin $\vec{\sigma}_R$ is coupled with the localized spin $\vec{S}_R$ according to Hund's rule $2J\vec{\sigma}_R \cdot \vec{S}_R$, yielding the state $S+\frac{1}{2}$ or $S-\frac{1}{2}$, depending upon the relative orientation of the two spins.

The interaction energy calculated by Anderson and Hasegawa[6] from a system of two atoms sharing one Zener electron always favors ferromagnetism, but their conclusion is somewhat misleading. If one more Zener electron is added, each atom will carry a single electron forming the states with $S+\frac{1}{2}$ and the interaction between the atoms disappears. Hence the interaction energy obviously depends on the density of Zener electrons. In a solid, an antiferromagnetic state might become stable, rather than the ferromagnetic state.

In this Letter, we shall show that the model described above yields a new mechanism for spin-polarized split bands responsible for ferromagnetism. To demonstrate it, we shall calculate the Green's function of the lattice. The Hamiltonian is given by[7]

$$\mathcal{H} = \sum_{R,R',\sigma} \epsilon_{RR'} C_{R\sigma}{}^{\dagger} C_{R'\sigma} - 2J \sum_{R} \vec{\sigma}_R \cdot \vec{S}_R + I \sum_{R} N_{R\uparrow} N_{R\downarrow}, \tag{1}$$

where $\epsilon_{RR}=0$ and $N_{R\sigma}=C_{R\sigma}{}^{\dagger}C_{R\sigma}$. To reduce the chances of finding two Zener electrons with opposite spins at the same atomic site, we have added the strong intra-atomic repulsive interaction $I\sum_R N_{R\uparrow} \times N_{R\downarrow}$ with $I \approx 5$–10 eV, which is dominant compared to the Hund's-rule splitting $J(2S+1)$ of the order of 1–2 eV. The bandwidth is supposed to be much smaller than I and rather comparable to $J(2S+1)$.

The form of the Hund's-rule interaction appears to be the same as the s-d interaction, and x electrons at an atomic site behave as if they are localized, even though they are the same type of d electrons as Zener electrons. The condition that atoms with fewer than x electrons become energetically unfavorable and do not appear has introduced this apparent constraint on the hopping motion of the electrons.

In a conventional problem of the s-d interaction, the conduction band is wide compared to the s-d interaction J and hence J is treated as a perturbation. Edwards[7] has calculated the interaction J clas-

sically so that ferromagnetism is always favored as long as J remains positive. To eliminate this difficulty he introduces, rather arbitrarily, an effective interaction J_{eff} which can become negative. In this paper the Hund's-rule splitting, being comparable to the hopping matrix elements $\epsilon_{RR'}$ of d electrons, cannot be regarded as a small perturbation or as a classical coupling. In particular, to preserve its atomic nature rigorously, we shall treat it together with the intra-atomic interaction term in the manner in which Hubbard calculated narrow bands.

The one-particle double-time Green's function

$$\langle\langle C_{R\sigma}; C_{R'\sigma}{}^{\dagger}\rangle\rangle = \langle\langle C_{R\sigma}N_{R\bar{\sigma}}{}^{(+)}; C_{R'\sigma}{}^{\dagger}\rangle\rangle + \langle\langle C_{R\sigma}N_{R\bar{\sigma}}{}^{(-)}; C_{R'\sigma}{}^{\dagger}\rangle\rangle,$$

may be calculated by the equation of motion:

$$\begin{aligned}(E-\delta I)\langle\langle C_{R\sigma}N_{R\bar{\sigma}}{}^{(\pm)}; C_{R'\sigma}{}^{\dagger}\rangle\rangle &= (2\pi)^{-1/2}\delta_{RR'}\langle N_{R\bar{\sigma}}{}^{(\pm)}\rangle + \textstyle\sum_{R''}\epsilon_{RR''}\langle\langle C_{R''\sigma}N_{R\bar{\sigma}}{}^{(\pm)}; C_{R'\sigma}{}^{\dagger}\rangle\rangle \\ &\quad - J\langle\langle \gamma_{\sigma}C_{R\sigma}N_{R\bar{\sigma}}{}^{(\pm)}S_{Rz} + C_{R\bar{\sigma}}N_{R\sigma}{}^{(\pm)}S_{R\mp}; C_{R'\sigma}{}^{\dagger}\rangle\rangle \\ &\quad + \gamma_{(\pm)}\textstyle\sum_{R''}(\epsilon_{RR''}\langle\langle C_{R\sigma}C_{R\bar{\sigma}}{}^{\dagger}C_{R''\bar{\sigma}}; C_{R'\sigma}{}^{\dagger}\rangle\rangle \\ &\quad - \epsilon_{R''R}\langle\langle C_{R\sigma}C_{R''\bar{\sigma}}{}^{\dagger}C_{R\bar{\sigma}}; C_{R'\sigma}{}^{\dagger}\rangle\rangle),\end{aligned} \tag{2}$$

where $N_{R\sigma}{}^{(+)} = N_{R\sigma}$, $N_{R\sigma}{}^{(-)} = 1 - N_{R\sigma}$, and $\bar{\sigma}$ is the opposite of spin σ. The equation for the Green's function, which appears in the third term on the right-hand side of Eq. (2), is

$$\begin{aligned}&(E+\gamma_{(\pm)}J-\delta I)\langle\langle \gamma_{\sigma}C_{R\sigma}N_{R\bar{\sigma}}{}^{(\pm)}S_{Rz} + C_{R\bar{\sigma}}N_{R\sigma}{}^{(\pm)}S_{R\mp}; C_{R'\sigma}{}^{\dagger}\rangle\rangle \\ &\quad = (2\pi)^{-1/2}\delta_{RR'}(\gamma_{\sigma}\langle N_{R\bar{\sigma}}{}^{(\pm)}S_{Rz}\rangle + \gamma_{(\pm)}\langle C_{R\bar{\sigma}}C_{R\sigma}{}^{\dagger}S_{R\mp}\rangle) + \textstyle\sum_{R''}\epsilon_{RR''}\langle\langle \gamma_{\sigma}C_{R''\sigma}N_{R\bar{\sigma}}{}^{(\pm)}S_{Rz} \\ &\qquad + C_{R''\bar{\sigma}}N_{R\sigma}{}^{(\pm)}S_{R\mp}; C_{R'\sigma}{}^{\dagger}\rangle\rangle - J\langle\langle C_{R\sigma}N_{R\bar{\sigma}}{}^{(\pm)}\vec{S}^{2}; C_{R'\sigma}{}^{\dagger}\rangle\rangle + \cdots.\end{aligned} \tag{3}$$

Here, $\gamma_{\sigma} = 1$ and $S_{R\mp} = S_{R-}$ for $\sigma = \uparrow$, and $\gamma_{\sigma} = -1$ and $S_{R\mp} = S_{R+}$ for $\sigma = \downarrow$, respectively; $\gamma_{(\pm)} = \pm 1$; $\delta = 1$ for $(\pm) = (+)$ and $\delta = 0$ for $(\pm) = (-)$; and $+\cdots$ is a term similar to the last term on the right-hand side of Eq. (2). Since $\vec{S}^2$ is a constant of motion, it can be replaced by its eigenvalue $S(S+1)$.

In the atomic limit, where the lattice parameter is infinite and $\epsilon_{RR'} = 0$, the above equations can be solved *exactly*, yielding the result

$$\langle\langle C_{R\sigma}; C_{R'\sigma}{}^{\dagger}\rangle\rangle = \frac{\delta_{RR'}}{2\pi}\left(\frac{1}{F} + \frac{1}{\Delta F}\right), \tag{4}$$

where

$$\frac{1}{F} = \frac{S+\gamma_{\sigma}M+1}{2S+1}\frac{1-n_{\bar{\sigma}}}{E+JS} + \frac{S-\gamma_{\sigma}M}{2S+1}\frac{1-n_{\bar{\sigma}}}{E-J(S+1)} + \frac{S+\gamma_{\sigma}M}{2S+1}\frac{n_{\bar{\sigma}}}{E-I+J(S+1)} + \frac{S-\gamma_{\sigma}M+1}{2S+1}\frac{n_{\bar{\sigma}}}{E-I-JS}, \tag{5}$$

and $n_{\sigma} \equiv \langle \boldsymbol{N}_{\sigma}\rangle$. The expression for $1/\Delta F$ is obtained from Eq. (5) by replacing the numerators by $\pm\langle C_{R\bar{\sigma}}C_{R\sigma}{}^{\dagger}S_{R\mp}\rangle \equiv T$. T will be small compared to S and will vanish when the localized spin $\vec{S}_R$ and the electron spin $\vec{\sigma}_R$ are parallel, that is, where $\gamma_{\sigma}M = S$.

The above result shows that if a single Zener electron appears at an atomic site and its spin $\vec{\sigma}_R$ and the localized spin $\vec{S}_R$ are parallel, they form the state $S+\frac{1}{2}$ with energy $-JS$. If they are not parallel, however, the probability of finding the state $S+\frac{1}{2}$ will be reduced to $A_1{}^0 = (S+\gamma_{\sigma}M+1-T)/(2S+1)$, and there will be a probability $A_2{}^0 = (S-\gamma_{\sigma}M+T)/(2S+1)$ of finding the state $S-\frac{1}{2}$ with energy $J(2S+1)$. Hence the first $NA_1{}^0$ Zener electrons will occupy the energy level $E_1 = -JS$, each forming the state $S+\frac{1}{2}$ at an atomic site; the next $NA_2{}^0$ electrons occupy the level $E_2 = J(S+1)$, creating the state $S-\frac{1}{2}$ at the remaining atomic sites. After every atom is filled with a single Zener electron, the next $N(S+\gamma_{\sigma}M+T)/(2S+1)$ electrons occupy the level $E_3 = I - J(S+1)$, and the last $N(S-\gamma_{\sigma}M+1-T)/(2S+1)$ electrons occupy the level $E_4 = I+JS$. When $\vec{\sigma}_R$ and the $\vec{S}_R$ are all parallel, the first N electrons go to level E_1, but if $\vec{\sigma}_R$ and the $\vec{S}_R$ are all antiparallel and $\gamma_{\sigma}M = -S$, only a small number of electrons can occupy E_1 and the majority of the first N electrons go to E_2, and so on. If the relative orientations of spins $\vec{\sigma}_R$ and $\vec{S}_R$ are random and if $\gamma_{\sigma}M \approx 0$, each level accepts roughly $\frac{1}{2}N$ electrons and the levels will be filled from the bottom. These are known results in atomic spectra.

At finite lattice constants, Eqs. (2) and (3) may be solved, provided that on the right-hand sides of

Eqs. (2) and (3) we decouple the Green's functions in the second terms and neglect the last terms involving four C's.

These treatments correspond to Hubbard's simplest approximation and will reproduce the main feature of the Hubbard-type strong correlation in narrow bands. The result is

$$\langle\langle C_{\vec{k}\sigma}; C_{\vec{k}'\sigma}^{\dagger}\rangle\rangle = \frac{\delta_{\vec{k}\vec{k}'}}{2\pi}\left(\frac{1}{F}+\frac{1}{\Delta F}\right)\frac{F}{F-\epsilon_{\vec{k}}}, \tag{6}$$

where $C_{\vec{k}\sigma}$ and $\epsilon_{\vec{k}}$ are the Fourier transforms of $C_{R\sigma}$ and $\epsilon_{RR'}$, respectively. Since the origin of the energy is fixed at the centroid of the band through the choice $\epsilon_{RR}=0$, roughly the first half of $\epsilon_{\vec{k}}$ will be negative and the rest positive as long as the hopping matrix elements between distant atoms decay exponentially.

If $J=0$, the resonant function F becomes exactly the same as in the Hubbard case and the band splits in two such that its lower band lies below $I(1-n_{\bar{\sigma}})$ and the upper band above $I(1-n_{\bar{\sigma}})$. For a finite J ($\ll I$), each of the Hubbard split bands will again split into two. The Hubbard lower band splits such that its lower sub-band remains below $J(\gamma_{\sigma}M+1)$. The splitting of the Hubbard upper band is also similar, yielding four sub-bands. To derive these results, let the sum of the last two terms on the right-hand side of Eq. (5) be denoted by $1/F_2(E)$. When $E\approx E_{\mathrm{low}}$, $F_2(E)$ will be a slowly varying function of E and will be small since I dominates over JS as well as over the bandwidth. The lower two sub-bands E_{low} of $F-\epsilon_{\vec{k}}=0$ may then be calculated by $F_1(E)-\epsilon_{\vec{k}'}=0$, where $1/F_1(E)$ denotes the first two terms on the right-hand side of Eq. (5) and $\epsilon_{\vec{k}}'=\epsilon_{\vec{k}}[1-\epsilon_{\vec{k}}/F_2(E)]^{-1}$ should be determined self-consistently. This reduced equation is exactly the same form as the Hubbard quadratic equation, yielding the Hubbard-type split bands:

$$E_{1,2}=-JS+\tfrac{1}{2}\left\{J(2S+1)+n_{\bar{\sigma}}^{(-)}\epsilon_{\vec{k}}'\pm\{[J(2S+1)+n_{\bar{\sigma}}^{(-)}\epsilon_{\vec{k}}']^2-4n_{\bar{\sigma}}^{(-)}\epsilon_{\vec{k}}'J(2S+1)A_1^{0}\}^{1/2}\right\}. \tag{7}$$

The same treatment can be extended to the Hubbard upper band.

The Green's function is then written in the form

$$\langle\langle C_{\vec{k}\sigma}; C_{\vec{k}'\sigma}^{\dagger}\rangle\rangle = \frac{\delta_{\vec{k}\vec{k}'}}{2\pi}\left(\frac{A_1 n_{\bar{\sigma}}^{(-)}}{E-E_1}+\frac{A_2 n_{\bar{\sigma}}^{(-)}}{E-E_2}+\frac{A_3 n_{\bar{\sigma}}}{E-E_3}+\frac{A_4 n_{\bar{\sigma}}}{E-E_4}\right), \tag{8}$$

where A_i's give the weights of the solutions E_i. In the narrow-band limit, A_i's are equal to the corresponding coefficients in Eq. (5), that is, $A_1\approx A_1^{0}$, etc. As the bandwidth increases, however, the values of A_i's deviate from A_i^{0}'s and become k dependent since $A_1\approx[A_1^{0}J(2S+1)-E_1]/(E_2-E_1)$, $A_2\approx[E_2-A_1^{0}J(2S+1)]/(E_2-E_1)$, etc.; but we find that the deviation is normally small as long as the bandwidth is smaller than $J(2S+1)$. As the bandwidth becomes wider and $E_1\approx A_1^{0}J(2S+1)$, we find $A_1\approx 0$ and $A_2\approx 1$ even if $A_1^{0}\gg A_2^{0}$ and vice versa. However, this happens only for a small number of electrons having $E_1\approx A_1^{0}J(2S+1)$, etc. For the majority of states $\vec{k}$, therefore, the conclusion obtained for the atomic limit will persist and the weight of the sub-bands will depend on the relative orientations of the electron spin $\vec{\sigma}_R$ and the localized spin $\vec{S}_R$.

Let us consider, for simplicity, cases with less than one Zener electron per atom and discuss the two sub-bands coming from the Hubbard lower band. Suppose that the localized spins $\vec{S}_R$ are aligned ferromagnetically along the z axis. For the spin-up Zener electrons, the weight of the lower sub-band will be dominant and the upper sub-band accepts only a small number of electrons. For the spin-down Zener electrons, the trend is reversed. As long as the number of Zener electrons, nN, is small, then most of them will occupy the spin-up lower sub-band, enhancing the magnetization already created by the localized spins $\vec{S}_R$. The energy spectra for the spin-up lower sub-band calculated by Eq. (7) are written approximately as $E_1=-JS+n_{\downarrow}^{(-)}\epsilon_{\vec{k}}$, where the spin-down sub-band is nearly empty and $n_{\downarrow}^{(-)}=1$. Since the lower half of $\epsilon_{\vec{k}}$ is negative, the total energy of the lattice will then be reduced by the optimum amount by the kinetic energy.

In case the localized spins $\vec{S}$ are randomly oriented, the weights of the lower and upper sub-bands for both spin-up and spin-down Zener electrons will become equal. The energy spectra for the lower sub-bands for both spins may be expanded as $E_1\approx -JS+\alpha n_{\bar{\sigma}}^{(-)}\epsilon_{\vec{k}'}+\cdots$, where $\alpha\lesssim\frac{1}{2}$ and $n_{\bar{\sigma}}^{(-)}=1-\frac{1}{2}n$. Hence, nN electrons will fill the spin-up and spin-down lower sub-bands equally, and the kinetic energy reduction of the lattice will be less than one half that of the fer-

romagnetic lattice. Thus the present model favors ferromagnetism when the density of Zener electrons is low. If the density of Zener electrons increases and both the lower and upper subbands are filled, that is, the case of one electron per atom, the energy difference between the ferromagnetic and nonmagnetic lattices disappears. Then a simple extension of our previous calculation[2] will lead to the conclusion that an antiferromagnetic sublattice structure yields a lower energy, illustrating the intricate dependence of magnetic ordering in the present model on the density of electrons.

The present model suggests that Hund's-rule coupling, rather than the Hartree-Fock field, is the key mechanism for the spin-polarized splitting of bands responsible for ferromagnetism in transition metals. The Hartree-Fock splitting assumed in the band theory of ferromagnetism is believed to be suppressed when the Wigner-type correlations are included, while the present mechanism is exact in the atomic limit.

Ferromagnetic materials such as Fe and Co have more than one $3d$ hole per atom and the Hund's-rule coupling must play an important role in the magnetic properties as discussed here. It is widely speculated[4] that $3d^8$ configurations in Ni are of crucial importance for its stability, suggesting that the present theory is also applicable to the ferromagnetism of Ni.

*Work performed under the auspices of the U. S. Atomic Energy Commission, of the Gruppo Nazionale di Struttura della Materia del Consiglio Nazionale delle Ricerche, Italy, and of the Istituto Nazionale di Fisica Nucleare, Italy.

†On leave of absence from Argonne National Laboratory during 1970–1971.

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Prominent Two-Body Effects in the Processes $p(^3\mathrm{He}, pd)p$ and $d(d, pd)n$

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(Received 30 August 1971)

A coincidence study of three-body breakup of the $^3\mathrm{He}+p$ and the $d+d$ system has been made with the multidetector system BOL at 69-MeV ^{3}He energy and 26-MeV deuteron energy. Strong contributions from quasi two-body reactions (final-state interaction and quasifree scattering) are found. The Watson-Migdal theory and the plane-wave impulse approximation model do not consistently explain the data. The discrepancies are particularly striking where different two-body mechanisms overlap.

The crucial feature of multiparticle nuclear reactions is the complicated dependence of the differential cross section on several kinematic variables, a major challenge to contemporary experimental techniques. In single-counter experiments, the cross section is implicitly integrated over a large part of the available phase space. Often this integration masks even prominent characteristics of the contributing reaction mechanisms. In more time-consuming, kinematically complete coincidence measurements, different processes can be optimally identified though they usually cover only a small region of the total phase space. The multidetector system BOL[1] allows one to investigate a large part of phase space, yet in a kinematically complete way. Thus an overall view of the reaction is obtained and, in addition, any desired detail can be investigated. Normal and deuterated polyethylene targets ($\simeq 2$ mg/cm^2) were bombarded by 69-MeV ^{3}He particles and 26-