

Exchange Narrowing of d Bands in Ferromagnets*

THOMAS WOLFRAM AND JOSEPH CALLAWAY

Department of Physics, University of California, Riverside, California

(Received February 21, 1962; revised manuscript received April 30, 1962)

A semiphenomenological Hamiltonian based on the generalized Hartree-Fock equations for a two-component spinor is developed which describes the interaction of an electron in the d band with the spin waves of a ferromagnet. Solutions to the effective Hamiltonian are examined in the tight-binding approximation using a self-consistent separation of the electron and spin-wave variables. The dynamic interaction of the electron with the spin waves gives rise to a band-narrowing factor $\exp(-\zeta)$ analogous to that obtained by Yamashita and Kurosawa for the polaron. ζ increases with temperature and estimates show that it may be on the order of unity for a typical ferromagnet at low temperatures.

I. INTRODUCTION

THE dynamic interaction of a d electron with the spin-wave system in a ferromagnet is quite similar qualitatively to the electron-phonon interaction in a polar crystal. A brief review of some feature of the electron-phonon interaction helps to make the similarity clear. In polar crystals, there is a strong interaction between the charge carriers and the lattice. The Hamiltonian for such a system consists of three terms: H_{el} , H_{int} , and H_{ph} . The electron (or hole) Hamiltonian H_{el} contains the electron kinetic energy and an effective one-electron periodic potential. The phonon component is H_{ph} , and H_{int} is the electron-phonon interaction term. The latter term is a function of the electron coordinates and usually linear in the lattice particle displacements.¹ When H_{int} is small it may be treated by perturbation methods and gives rise to electron-phonon scattering. If H_{int} is large, perturbation techniques are not valid and the effect of the lattice on the electron wavefunction must be considered in the lowest order of approximation. The electron-lattice interaction causes a relaxation of the lattice around the electron. The unit consisting of the electron and the lattice distortion surrounding it constitutes a quasi-particle called the polaron. A large interaction tends to wash out the electronic band structure. More precisely, the band width is reduced by a factor $\exp(-\zeta)$.^{2,3} The damping exponent ζ increases with the number of phonons excited and hence with temperature.

The interaction of a d electron in a ferromagnet with spin waves is analogous to the polaron problem if we consider the electron and spin waves to be separate subsystems. The Hamiltonian is again the sum of three terms, H_{el} , $H_{s.w.}$, and H_{int} . Here H_{el} is a one-electron Hamiltonian including the electron kinetic energy and the effective electrostatic potential. The Heisenberg spin Hamiltonian $H_{s.w.}$ describes the coupling of the spins on neighboring sites. The simple isotropic spin

Hamiltonian can be written in a quadratic form completely analogous to the lattice Hamiltonian H_{ph} of the polaron problem.⁴ H_{int} is an effective intra-atomic exchange interaction proportional to the scalar product of the d -electron spin and the total spin of the site, and therefore couples the electron to the spin-wave system. In the polaron problem the system can achieve a lower energy by distortion of the lattice and localization of the charge carrier. A similar effect has been suggested by Zener⁵ for an electron interacting with the spin waves of a ferromagnet. In this paper we shall develop a semiphenomenological Hamiltonian for the investigation of the dynamic interaction of a d electron with the spin waves of a ferromagnet. In particular we show that a significant narrowing of the electron energy band can occur.

II. THE GENERALIZED HARTREE-FOCK EQUATIONS

The Hartree-Fock equations for an n -electron solid system are usually written assuming that each electron of the system has its spin quantized parallel or antiparallel to a given direction. There are many circumstances in which this simplifying assumption is too restrictive. If spin-orbit coupling is included in the Hamiltonian, one cannot in general find solutions which are one-component spinors. In this case a single component of the spin of an individual electron cannot be considered to be a constant of the motion and two-component spinors must be employed. Moreover, even in the absence of spin-orbit interaction the solutions of the Hartree-Fock equations need not be one-component spinors. Thompson⁶ has shown that the full implications of the Hartree-Fock equations can be realized only when this restriction is abandoned, and one considers a more general class of solutions—two component spinors, in which the spin of the individual electron is no longer a constant of the motion. Thompson has investigated this problem in detail and subject to

* Supported by the Air Force Office of Scientific Research.

¹ S. I. Pekar, *Untersuchungen Über die Electronenthorie der Kristalle* (Akademia-Verlag, Berlin, 1954).

² J. Yamashita and T. Kurosawa, *J. Phys. Chem. Solids* **5**, 34 (1958).

³ T. Holstein, *Ann. Phys. (New York)* **8**, 325 (1959); **8**, 343 (1959).

⁴ J. Van Kranendonk and J. H. Van Vleck, *Revs. Modern Phys.* **30**, 1 (1958).

⁵ C. Zener, *J. Phys. Chem. Solids* **8**, 26 (1959).

⁶ E. D. Thompson, Ph.D. thesis, Massachusetts Institute of Technology, June 1960 (unpublished).

certain reasonable assumptions⁷ the generalized two-component Hartree-Fock solutions are found to satisfy the equations

$$\{(\hbar^2/2m) + V(\mathbf{r}) + V_{\text{el}}(\mathbf{r}) - \frac{1}{2}G^i[\rho(\mathbf{r}) + \mathbf{M}(\mathbf{r}) \cdot \boldsymbol{\sigma}]\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r}), \quad (1)$$

where $\mathbf{M}(\mathbf{r})$ is the magnetization density at the point \mathbf{r} due to all the electrons, $\boldsymbol{\sigma}$ is the Pauli spin operator, $\rho(\mathbf{r})$ is the charge density, and $V(\mathbf{r})$ is the effective potential due to the ion cores. $V_{\text{el}}(\mathbf{r}) = \int d\mathbf{r}' U(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}')$, where $U(\mathbf{r}, \mathbf{r}')$ is a Coulomb or screened Coulomb potential at \mathbf{r} due to charge at \mathbf{r}' . G^i is a constant which is allowed to be different for different orbitals φ_i and has to be determined self-consistently. A spin-orbit interaction may be added to this effective Hamiltonian and we shall do so in the next section.

III. THE PHENOMENOLOGICAL ONE-ELECTRON HAMILTONIAN

In this paper we are interested in obtaining a semi-phenomenological one-electron Hamiltonian based on Eq. (1), which includes the effect of the coherent magnetization fluctuations on the electronic solutions. At the same time we wish to write the effective Hamiltonian in such a form that a tight-binding scheme is appropriate. It can be shown⁶ that Eq. (1) admits self-consistent solutions in which the charge density is a periodic function in the lattice translations. This assumption allows the effective Hamiltonian to be written as a sum of local potentials. The magnetization density $\mathbf{M}(\mathbf{r})$ can then be written as a sum of local magnetization densities associated with the atomic sites. Each local magnetization is assumed proportional to the net spin on the site. The spin coupling term of (1) then has the form:

$$\frac{1}{2}G^i \mathbf{M}(\mathbf{r}) \cdot \boldsymbol{\sigma} = \sum_j G^i(\mathbf{r} - \mathbf{R}_j) \mathbf{S}_e \cdot \mathbf{S}_j, \quad (2)$$

where \mathbf{S}_e is the vector operator for the spin of the electron and \mathbf{S}_i the spin of the site at coordinate \mathbf{R}_i . With these assumptions the Hartree-Fock one-electron Hamiltonian takes the form

$$H = \frac{\hbar^2}{2m} + \sum_j \left[V^i(\mathbf{r} - \mathbf{R}_j) + \frac{1}{2mc^2} \mathbf{S}_e \cdot \nabla V^i(\mathbf{r} - \mathbf{R}_j) \times \mathbf{p} - G^i(\mathbf{r} - \mathbf{R}_j) \mathbf{S}_e \cdot \mathbf{S}_j \right]. \quad (1a)$$

In (1a) all of the spin-independent potentials have been incorporated into the term $\sum_j V^i(\mathbf{r} - \mathbf{R}_j)$ and in addition a spin-orbit interaction has been inserted. The function $G(\mathbf{r} - \mathbf{R}_i)$ is like an exchange potential and is expected to be large in the neighborhood of \mathbf{R}_i . Equation (1a) is a natural consequence of the generalized Hartree-Fock equations (1) within the validity of the assumption made concerning the magnetization density. However,

we shall see in the following discussion that this effective Hamiltonian must be supplemented in a phenomenological way with an additional essential term.

It follows from many-body theory that we can define energy bands in a solid by considering the difference in energy between the ground state of an n -body system and that of an $(n \pm 1)$ -particle system in which an additional electron has been added to (or removed from) a state of wave vector \mathbf{k} .⁸ In the present case we, add the particle to a localized orbital on a site designated by a lattice vector \mathbf{R}_i , and then form the appropriate linear combination with coefficients $\exp(i\mathbf{k} \cdot \mathbf{R}_i)$. An excess electron in a ferromagnet will, however, interact with the spin-wave system. As has been discussed by Thompson,⁶ if an excess electron travels through a ferromagnet with the expectation value of its spin inclined at an angle to the direction of magnetization of the crystal, a torque will be exerted on the electron, causing its spin to precess about the magnetization. Also, the subject electron exerts a torque on the other electrons of the crystal and as a result of conservation of total angular momentum, the net magnetization of the crystal will precess. This interaction is contained in equation (1a) in the coupling term $\mathbf{S}_e \cdot \mathbf{S}_i$. This term may be written in the form:

$$G(\mathbf{r} - \mathbf{R}_i) \mathbf{S}_e \cdot \mathbf{S}_i = G(\mathbf{r} - \mathbf{R}_i) [\mathbf{S}_{ez} \mathbf{S}_{iz} + \frac{1}{2}(\mathbf{S}_e^+ \mathbf{S}_i^- + \mathbf{S}_e^- \mathbf{S}_i^+)], \quad (3)$$

where $\mathbf{S}_e^\pm = (\mathbf{S}_{ex} \pm i\mathbf{S}_{ey})$ and $\mathbf{S}_i^\pm = (\mathbf{S}_{ix} \pm i\mathbf{S}_{iy})$. The first term can be interpreted as the usual exchange coupling which tends to align the spin of the electron parallel to the net spin of the site. This coupling perturbs the spin-wave system, but does not introduce any spin deviations in first order. This term will be referred to as the static interaction. The second term is of most interest to us since it contains operators which raise or lower the spin components, and thus couples the electron dynamically to the spin waves. We now examine these interactions in more detail. We neglect spin-orbit coupling and place the electron on site i . Suppose that the crystal is in its ground state so that \mathbf{S}_{iz} has its maximum value, S . There are two possible cases to be examined. In the case in which the electron spin is parallel to \mathbf{S}_i , the dynamic coupling term will vanish since neither spin can be raised. The static term will, however, be present. This static interaction can be pictured in a semiclassical model⁹ in which, in the absence of the excess electron, the precessional cone angle made by the site is

$$\sin\theta = S[S(S+1)]^{-1/2}. \quad (4)$$

When the extra electron couples parallel to form a spin vector whose magnitude is $[(S \pm S_e)(S \pm S_e + 1)]^{1/2}$, the

⁸ J. C. Phillips, Phys. Rev. **123**, 420 (1961).

⁷ The assumptions made amount to the requirement that the exchange interaction can be represented by an exchange potential.

⁹ A semiclassical discussion of spin waves has been given by F. Keffer, H. Kaplan, and Y. Yafet [J. Am. Phys. **21**, 250 (1953)].

maximum alignment for this new vector gives a cone angle:

$$\sin\theta' = (S \pm S_e) [(S \pm S_e)(S \pm S_e + 1)]^{-1/2}. \quad (5)$$

For reasonable values of S , θ and θ' can be significantly different. In the case of parallel alignment the cone angle is decreased and due to the increase in the number of majority spins the effective interatomic exchange with neighboring sites is increased. Classically we would expect that the system could respond by decreasing the cone angle at each site by a small amount. This cannot, however, be the case in quantum mechanics since these spins have already attained the maximum orientation allowed. We shall see to first order the static term increases the spin-wave frequencies. If there are spin deviations present in the system then the static term can in second order couple dynamically and it will be shown later that this occurs by the transfer of magnons between different spin-wave modes. Also if the spin S_i does not have its maximum orientation (the ferromagnet is not in its ground state), then of course the dynamic terms of the coupling operator will not vanish.

In the second case the excess spin is coupled oppositely to S_i . Then the electrons will always interact dynamically with the spin-wave system. Even if the ferromagnet is in its ground state (that is at absolute zero) the term $S_i^- S_e^+$ will not vanish. Therefore at low temperatures it appears that there may be a considerably larger dynamic coupling of electrons in the spin "down" band than for electrons in the spin "up" band. When spin-orbit effects are included then the classification of spin "up" or "down" is even less exact and the dynamic coupling need not vanish in either case.

We have seen that an electron traveling through a ferromagnetic crystal will in general couple to the spin-wave system. It perturbs and is perturbed by the spin waves. The wavefunction which describes an electron traveling through the crystal should include the perturbation of the spin-wave system. Therefore, we consider two-component electronic wavefunctions of the form

$$\varphi_i(\mathbf{r}, S_e; S_1, S_2, \dots, S_N), \quad (6)$$

which depend not only upon the electron coordinate but upon the state of the spin system as well.¹⁰ We must also add to the effective Hamiltonian (1a) a term which describes the spin state of the crystal as a whole. We are therefore lead to add to (1a) the Heisenberg spin Hamiltonian. We then postulate as our phenomenological one-electron Hamiltonian:

¹⁰ The introduction into a one-electron wavefunction of a parametric dependence on other electrons is not an innovation. A generalization of the Hartree-Fock one-electron functions of this sort was introduced by Wigner in order to account for the correlation energy of electrons with opposite spins. E. Wigner and F. Seitz, *Phys. Rev.* **46**, 509 (1934), and also E. Wigner, *ibid.* **46**, 1002 (1934).

$$H_{\text{eff}} = \frac{p^2}{2m} + \sum_i \left[V(\mathbf{r} - \mathbf{R}_i) - G(\mathbf{r} - \mathbf{R}_i) \mathbf{S}_e \cdot \mathbf{S}_i + \frac{1}{2mc^2} \mathbf{S}_e \cdot \nabla V(\mathbf{r} - \mathbf{R}_i) \times \mathbf{p} \right] - 2A \sum_{\text{nei}} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (7)$$

In (7) the sum over "nei" represents a sum over all neighboring pairs of site spins.

A basic motivation for the development of the Hartree-Fock equations introduced by Thompson was the idea that an electron both perturbs and is perturbed by spin waves. In Thompson's work a side condition that the magnetization density varied according to a classical spin wave was introduced. The magnetization spin wave was then inserted directly into equation (1) for $M(\mathbf{r})$. However, since the effective Hartree-Fock Hamiltonian does not contain the spin-wave Hamiltonian the reaction on the spin wave is quite indirect.

The energy band calculation is made in the tight binding approximation. We take the unperturbed functions to be eigenfunctions of the local Hamiltonian H^0 .

$$H_i^0 = \frac{p^2}{2m} + V(\mathbf{r} - \mathbf{R}_i) - G(\mathbf{r} - \mathbf{R}_i) \mathbf{S}_e \cdot \mathbf{S}_i + \frac{1}{2mc^2} \mathbf{S}_e \cdot \nabla V(\mathbf{r} - \mathbf{R}_i) \times \mathbf{p} - 2A \sum_{\text{nei}} \mathbf{S}_i \cdot \mathbf{S}_j. \quad (8)$$

The intra-atomic exchange can be expected to be large compared to the interatomic exchange which is expressed by the spin-wave Hamiltonian. In what follows the spin waves will be treated in the "harmonic approximation"⁴ and the magnons will be treated as Bosons. The interaction or attraction of spin deviations and higher order correction terms will be ignored.¹¹

The site spins can be transformed into spin-wave operators by the relations,¹²

$$\begin{aligned} \mathbf{S}_{iz} &= S - \mathbf{a}_i^* \mathbf{a}_i, \\ \mathbf{S}_i^+ &= (2S)^{1/2} \mathbf{a}_i, \\ \mathbf{S}_i^- &= (2S)^{1/2} \mathbf{a}_i^*, \\ \mathbf{a}_k &= (N)^{-1/2} \sum_i \exp(-i\mathbf{k} \cdot \mathbf{R}_i) \mathbf{a}_i, \end{aligned} \quad (9)$$

where N is the total number of atoms in the crystal, S is the maximum magnetic quantum number, and \mathbf{a}_k and \mathbf{a}_k^* are magnon annihilation and creation operators for the spin-wave mode with propagation vector \mathbf{k} . H^0 , when expressed in terms of these spin wave operators, takes the form:

$$\begin{aligned} H_i^0 &= p^2/2m + V(\mathbf{r} - \mathbf{R}_i) - \mathbf{S}_e G(\mathbf{r} - \mathbf{R}_i) \\ &\times \{ S - N^{-1} \sum_{k,k'} \mathbf{a}_k^* \mathbf{a}_{k'} \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_i] \} \\ &- \frac{1}{2} G(\mathbf{r} - \mathbf{R}_i) (2S/N)^{1/2} \sum_k [\mathbf{S}_e^+ \mathbf{a}_k^* \exp(i\mathbf{k} \cdot \mathbf{R}_i) \\ &+ \mathbf{S}_e^- \mathbf{a}_k \exp(-i\mathbf{k} \cdot \mathbf{R}_i)] + \sum_k \mathbf{a}_k^* \mathbf{a}_k \hbar \omega_k^0 \\ &+ E_s^0 + (1/2mc^2) \mathbf{S}_e \cdot \nabla V(\mathbf{r} - \mathbf{R}_i) \times \mathbf{p}, \end{aligned} \quad (10)$$

¹¹ F. J. Dyson, *Phys. Rev.* **102**, 1217 (1956).

¹² T. Holstein and H. Primakoff, *Phys. Rev.* **58**, 1098 (1940).

where $\hbar\omega_k^0 = 2AS[z - \sum_R \cos(\mathbf{k} \cdot \mathbf{R})]$ and $E_s^0 = -NS^2Az$. The sum over \mathbf{R} is a sum over the z vectors \mathbf{R} that connect an atom with its z nearest neighbors. \mathbf{S}_{ez} is the z component of the spin operator and \mathbf{S}_e^+ and \mathbf{S}_e^- are spin raising and lowering operators defined earlier. The terms involving products of the spin raising and lowering operators multiplied by spin-wave annihilation or creation operators are capable of straightforward interpretation—the electron spin is flipped and at the same time a spin deviation is annihilated or created in the spin-wave system. The term containing the product of spin-wave annihilation and creation operators, however, is not as easy to interpret. Let us first separate it into two contributions.

$$\begin{aligned} S_{ez}G(\mathbf{r}-\mathbf{R}_i) & [N^{-1} \sum_{k,k'} \mathbf{a}_k^* \mathbf{a}_{k'} \exp[i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_i]] \\ & = N^{-1} \mathbf{S}_{ez}G(\mathbf{r}-\mathbf{R}_i) \sum_k \mathbf{a}_k^* \mathbf{a}_k \\ & \quad + N^{-1} \mathbf{S}_{ez} \sum_{k,k',k \neq k'} \mathbf{a}_k^* \mathbf{a}_{k'} \exp[i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_i]. \end{aligned} \quad (11)$$

The first part of this sum may be combined with the term $-SS_{ez}G(\mathbf{r}-\mathbf{R}_i)$ of (10) to give

$$-(S - N^{-1} \sum_k \mathbf{a}_k^* \mathbf{a}_k) \mathbf{S}_{ez}G(\mathbf{r}-\mathbf{R}_i). \quad (12)$$

This operator may be interpreted as an exchange polarization operator. If the coupling introduces only small perturbations into the spin-wave system then we have

$$\sum_k \mathbf{a}_k^* \mathbf{a}_k \approx \sum_k \eta_k = \eta, \quad (13)$$

where η is the total number of spin deviations in the spin-wave system. (The spin-wave formalism is valid only when $S \gg \eta/N$.) The average number of spin deviations per lattice site is $\eta/N = \bar{\eta}$ so that the polarization operator reduces to

$$-(S - \bar{\eta}) \mathbf{S}_{ez}G(\mathbf{r}-\mathbf{R}_i). \quad (14)$$

If we now sum this over all the sites we will obtain the expectation value of the original operator in Eq. (1a):

$$\langle \sum_i G(\mathbf{r}-\mathbf{R}_i) \mathbf{S}_e \cdot \mathbf{S}_i \rangle = \sum_i (S - \bar{\eta}) \mathbf{S}_{ez}G(\mathbf{r}-\mathbf{R}_i). \quad (14a)$$

Thus the first term of (11) contains the first-order effects of the static interaction. As mentioned earlier in Sec. III, the static interaction is dynamic in second order. The second sum of Eq. (11) may be interpreted as follows. When spin deviations are present in the system, then the change in the precessional angle at the site due to the excess electron acts as a scattering mechanism. Since the static interaction is diagonal in the spin of the site, magnons cannot be created or annihilated because of conservation of spin. What can happen, however, is that an existing magnon with wavevector \mathbf{k}' is annihilated (or created) at the site of increased (or decreased) spin alignment with the simultaneous creation (or annihilation) of a magnon with wavevector \mathbf{k} . This process is described by the term $N^{-1} \sum_{k \neq k'} \mathbf{a}_k^* \mathbf{a}_{k'} \exp[i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{R}_i]$ and may be

thought of as a kind of “impurity” scattering of spin waves. It is obviously a second order process and we shall neglect its contribution.

A self-consistent field problem is really implied by Eq. (10). It is necessary in principle to calculate the potentials $V(\mathbf{r})$ and $G(\mathbf{r})$ from the electron wavefunctions including those being studied. These complications will be neglected here and the functions U and G will be treated instead as fixed potentials.

We shall employ a procedure analogous to that used by Yamashita² (in the polaron problem) in order to obtain eigenfunctions of H^0 . We choose, as a trial eigenfunction a product of a two-component spinor function of the electronic coordinates and spin Φ , and a function X of the spin-wave variables, which are symbolized by \mathbf{Q} .

$$\Psi(\mathbf{r}-\mathbf{R}_i; \mathbf{Q}) = \Phi(\mathbf{r}-\mathbf{R}_i) X(\mathbf{Q}) = \begin{pmatrix} \phi_1(\mathbf{r}-\mathbf{R}_i) \\ \phi_2(\mathbf{r}-\mathbf{R}_i) \end{pmatrix} X(\mathbf{Q}). \quad (15)$$

The usual variational procedure¹³ is employed to minimize the energy of the system subject to the normalization conditions

$$\begin{aligned} \int \Phi^*(\mathbf{r}-\mathbf{R}_i) \Phi(\mathbf{r}-\mathbf{R}_i) d\tau &= 1, \\ \langle X(\mathbf{Q}) | X(\mathbf{Q}) \rangle &= 1. \end{aligned} \quad (16)$$

The integration over τ includes a sum over the spin indices. The variations of X^* and Φ^* give the self-consistent equations

$$(H_{el} + \langle X(\mathbf{Q}) | H_{int} | X(\mathbf{Q}) \rangle) \Phi = E^0 \Phi, \quad (17)$$

$$\left(H_{s.w.} + \int \Phi^* H_{int} \Phi d\tau \right) X = \lambda X, \quad (18)$$

where E^0 and λ are Lagrange multipliers arising from the subsidiary conditions (16). In (17) and (18) the following notation has been introduced:

$$\begin{aligned} H_{el} &= p^2/2m + V(\mathbf{r}-\mathbf{R}_i) - SS_{ez}G(\mathbf{r}-\mathbf{R}_i) \\ & \quad + (1/2mc^2) \mathbf{S}_e \cdot \nabla V(\mathbf{r}-\mathbf{R}_i) \times \mathbf{p}, \end{aligned} \quad (19)$$

$$\begin{aligned} H_{int} &= \sum_k [N^{-1} \mathbf{a}_k^* \mathbf{a}_k - \frac{1}{2} \mathbf{S}_e + (2S/N)^{1/2} \mathbf{a}_k^* \exp(i\mathbf{k} \cdot \mathbf{R}_i) \\ & \quad - \frac{1}{2} \mathbf{S}_e - (2S/N)^{1/2} \mathbf{a}_k \exp(-i\mathbf{k} \cdot \mathbf{R}_i)] \\ & \quad \times G(\mathbf{r}-\mathbf{R}_i), \end{aligned} \quad (20)$$

$$H_{s.w.} = \sum_k \mathbf{a}_k^* \mathbf{a}_k \hbar\omega_k^0, \quad (21)$$

and we have set $E_s^0 = 0$ for convenience. Equation (17) is an effective Schrödinger equation for a d electron moving in a self-consistent exchange potential averaged over the spin waves. Similarly (18) represents the effective spin-wave equation including a perturbation from the exchange potential averaged over the electron wavefunction. These self-consistent equations implicitly assume that an adiabatic approximation is applicable.

¹³ H. Frohlich, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1953), Vol. 3, p. 325.

IV. THE PERTURBED SPIN-WAVE FUNCTIONS

In this section we diagonalize the modified spin-wave Hamiltonian. The perturbed spin-wave functions are then expanded in terms of the unperturbed spin-wave functions. To begin with we must evaluate the perturbation term $\int \Phi^* H_{\text{int}} \Phi d\tau$. Substituting from (15) for Φ and from (20) for H_{int} and performing the integration, we obtain the effective perturbation:

$$\int \Phi^* H_{\text{int}} \Phi d\tau = N^{-1} (J_{11} - J_{22}) \sum_k \mathbf{a}_k^* \mathbf{a}_k - J_{12} (2S/N)^{1/2} \sum_k \mathbf{a}_k^* \exp(i\mathbf{k} \cdot \mathbf{R}_i) - J_{12}^* (2S/N)^{1/2} \sum_k \mathbf{a}_k \exp(-i\mathbf{k} \cdot \mathbf{R}_i), \quad (22)$$

where

$$J_{11} = (1/2) \int |\phi_1|^2 G(\mathbf{r} - \mathbf{R}_i) d\tau, \quad (23)$$

$$J_{22} = (1/2) \int |\phi_2|^2 G(\mathbf{r} - \mathbf{R}_i) d\tau, \quad (24)$$

$$J_{12} = (1/2) \int \phi_1^* G(\mathbf{r} - \mathbf{R}_i) \phi_2 d\tau. \quad (25)$$

The perturbed spin wave Hamiltonian (18) is easily brought into diagonal form by the transformations

$$\omega_k = \omega_k^0 [1 + (J_{11} - J_{22})/N\hbar\omega_k^0], \quad (26)$$

$$\mathbf{b}_k = \mathbf{a}_k + \alpha_k(\mathbf{R}_i), \quad (26a)$$

$$\alpha_k(\mathbf{R}_i) = -(2S/N)^{1/2} (J_{12}/\hbar\omega_k) \exp(i\mathbf{k} \cdot \mathbf{R}_i). \quad (26b)$$

Equation (18) now takes the form

$$[\sum_k (\mathbf{b}_k^* \mathbf{b}_k - |\alpha_k|^2 \hbar\omega_k) X(Q) = \lambda X(Q). \quad (27)$$

This is the equation for a set of displaced harmonic oscillators with

$$X(Q) = \prod_k \chi(n(k), \mathbf{R}_i), \quad (28)$$

$$\lambda = \sum_k \lambda_k = \sum_k [n(k) - |\alpha_k|^2] \hbar\omega_k.$$

The $\chi(n(k), \mathbf{R}_i)$ may be expanded in terms of the unperturbed spin-wave solutions $\chi^0(n(k))$. Second-order perturbation gives the wavefunction correct to terms of order N^{-1} and normalized up to terms in N^{-2} .

$$\begin{aligned} \chi(n(k), \mathbf{R}_i) = & \{1 - \frac{1}{2} [2n(k) + 1] |\alpha_k|^2\} \chi^0(n(k)) \\ & + [n(k)]^{1/2} \alpha_k^* (\mathbf{R}_i) \chi^0(n(k) - 1) \\ & - [n(k) + 1]^{1/2} \alpha_k (\mathbf{R}_i) \chi^0(n(k) + 1) \\ & + \frac{1}{2} [\alpha_k^* (\mathbf{R}_i)]^2 \{[n(k)] [n(k) - 1]\}^{1/2} \chi^0(n(k) - 2) \\ & + \frac{1}{2} [\alpha_k (\mathbf{R}_i)]^2 \{[n(k) + 1] [n(k) + 2]\}^{1/2} \chi^0(n(k) + 2). \end{aligned} \quad (29)$$

The $\chi^0(n(k))$ satisfy the following equations:

$$\begin{aligned} \mathbf{a}_k^* \mathbf{a}_k \chi^0(n(k)) &= n(k) \chi^0(n(k)), \\ \mathbf{a}_k^* \chi^0(n(k)) &= [n(k) + 1]^{1/2} \chi^0(n(k) + 1), \\ \mathbf{a}_k \chi^0(n(k)) &= [n(k)]^{1/2} \chi^0(n(k) - 1), \\ \langle \chi^0(n(k)) | \chi^0(n'(k')) \rangle &= \delta_{n, n'} \delta_{k, k'}. \end{aligned} \quad (30)$$

The states defined by (30) are rigorously orthogonal and properly normalized for small $n(k)$ or at low temperatures. The effect of the nonorthogonality for larger numbers of magnons has been discussed by Dyson.¹¹ However, these complications will be ignored since our model applies only in the temperature range for which the spin states obey (30). From Eq. (28) we see that at $T=0^\circ\text{K}$ the perturbed spin-wave system has an energy lower than the unperturbed system by an amount

$$\sum_k |\alpha_k|^2 \hbar\omega_k. \quad (31)$$

The spin wave function for the crystal as a whole will of course be a linear combination of functions of the type (29) with the electron at each of the sites. However, since (31) is independent of \mathbf{R}_i it follows that this is the amount by which the spin-wave energy will be lowered for the crystal as a whole.

V. EFFECTIVE ONE-ELECTRON HAMILTONIAN

Since the perturbed spin-wave equation has been solved, we are now in a position to evaluate the interaction H_{int} averaged over the spin waves. The integration is easily accomplished using the relations (30). The result is (neglecting terms of order N^{-2})

$$\begin{aligned} \langle X | H_{\text{int}} | X \rangle &= [\mathbf{S}_{ez} \eta / N - (S/N) (J_{12}^* \mathbf{S}_e^+ + J_{12} \mathbf{S}_e^-) \sum_k (\hbar\omega_k)^{-1}] \\ &\quad \times G(\mathbf{r} - \mathbf{R}_i), \end{aligned} \quad (32)$$

and the effective tight-binding Hamiltonian is

$$\begin{aligned} & \frac{p^2}{2m} + U(\mathbf{r} - \mathbf{R}_i) \\ &= \frac{p^2}{2m} + V(\mathbf{r} - \mathbf{R}_i) - G(\mathbf{r} - \mathbf{R}_i) (S - \eta) \mathbf{S}_{ez} \\ &\quad - [(S/N) (J_{12}^* \mathbf{S}_e^+ + J_{12} \mathbf{S}_e^-) \sum_k (\hbar\omega_k)^{-1}] \\ &\quad \times G(\mathbf{r} - \mathbf{R}_i) + \frac{1}{2mc^2} \mathbf{S}_e \cdot \nabla V(\mathbf{r} - \mathbf{R}_i) \times \mathbf{p}. \end{aligned} \quad (33)$$

We note that in addition to the usual static exchange potential contained in the third term there is an additional attractive exchange potential represented by the fourth term. This additional coupling term arises from the dynamic interaction of the electron with the spin waves and will increase localization of the solutions of Φ of (15). This additional localization of the electron will depend upon the degree of excitation of the spin waves, and we shall see that a band narrowing arises which increases with the number of magnons, and hence with temperature.

VI. BAND NARROWING IN A FERROMAGNET

In this section we form Bloch wavefunctions from the localized functions Φ of (15) and show that a band

narrowing results from the exchange interaction. The effective Hamiltonian for the energy band problem contains two terms, the electron kinetic energy and the sum of the effective tight-binding potentials of (33):

$$H_{\text{E.B.}} = p^2/2m + \sum_i U(\mathbf{r} - \mathbf{R}_i). \quad (34)$$

The energy band problem consists of finding solutions to the equation

$$H_{\text{E.B.}} \psi_q = E(q) \psi_q, \quad (35)$$

where \mathbf{q} is the electron propagation vector. We construct the Bloch functions ψ_q from the localized solutions $\Phi(\mathbf{r} - \mathbf{R}_i)$. A general localized function contains a superposition of spin functions with different quantum numbers

$$\tilde{\Psi}(\mathbf{r} - \mathbf{R}_i) = \Phi(\mathbf{r} - \mathbf{R}_i) \sum_{\{n(k)\}} B(\{n(k)\}, \mathbf{R}_i) \times \prod_k \chi(n(k), \mathbf{R}_i), \quad (36)$$

in which the sum is over all possible combinations of spin-wave quantum numbers and $B(\{n(k)\}, \mathbf{R}_i)$ is the amplitude coefficient for a given set $\{n(k)\}$ which can depend upon the site. The generalized Bloch functions are then linear combinations of the $\tilde{\Psi}$:

$$\psi_q = N^{-1/2} \sum_i \exp(i\mathbf{q} \cdot \mathbf{R}_i) \tilde{\Psi}(\mathbf{r} - \mathbf{R}_i). \quad (37)$$

This type of generalized Bloch wave will be important in determining the transport properties of the d electrons in a ferromagnet. At present we are not concerned with the transport properties and therefore for simplicity we will assume that the set of spin quantum numbers is independent of the site. The localized functions are taken to be

$$\Psi(\mathbf{r} - \mathbf{R}_i) = \Phi(\mathbf{r} - \mathbf{R}_i) \prod_k \chi(n(k), \mathbf{R}_i), \quad (38)$$

and the corresponding Bloch functions are

$$\psi_q = N^{-1/2} \sum_i \exp(i\mathbf{q} \cdot \mathbf{R}_i) \Psi(\mathbf{r} - \mathbf{R}_i), \quad (39)$$

where $\{n(k)\}$ is the same for all R_i . We now proceed in the usual way to calculate the energy as a function of the electron propagation vector \mathbf{q} , neglecting the change in normalization of the wavefunction produced by nonzero overlap integrals.

$$\begin{aligned} E(q) &= \int \left\langle \psi_q \left| \frac{p^2}{2m} + \sum_i U(\mathbf{r} - \mathbf{R}_i) \right| \psi_q \right\rangle d\tau \\ &= N^{-1} \sum_{i,j} \exp[i\mathbf{q} \cdot (\mathbf{R}_i - \mathbf{R}_j)] \int \Phi^*(\mathbf{r} - \mathbf{R}_j) \\ &\quad \times \left[\frac{p^2}{2m} + \sum_i U(\mathbf{r} - \mathbf{R}_i) \right] \Phi(\mathbf{r} - \mathbf{R}_i) d\tau \\ &\quad \times \prod_k \langle \chi(n(k), \mathbf{R}_j) | \chi(n(k), \mathbf{R}_i) \rangle. \end{aligned} \quad (40)$$

If only the nearest-neighbor matrix elements are in-

cluded, we obtain

$$E(q) = E^0 + \sum_{\mathbf{R}} \exp(i\mathbf{q} \cdot \mathbf{R}) \mathcal{E}(\mathbf{R}) \times \prod_k \langle \chi(n(k), 0) | \chi(n(k), \mathbf{R}) \rangle, \quad (41)$$

in which

$$\mathcal{E}(\mathbf{R}) = \int \Phi^*(\mathbf{r}) \left[\sum_{i \neq 0} U(\mathbf{r} - \mathbf{R}_i) \right] \Phi(\mathbf{r} - \mathbf{R}) d\tau, \quad (42)$$

and E^0 is given by (17). The sum over \mathbf{R} is a sum over the z vectors \mathbf{R} that connect the atom at the origin with its z nearest neighbors. If the spin functions χ were independent of the site, (41) would reduce to the usual tight-binding expression for the electron energy as a function of the electron propagation vector \mathbf{q} . The spin-wave integrals in (41) can be calculated with the use of the expression for χ given in (29),

$$\begin{aligned} \langle \chi(n(k), 0) | \chi(n(k), \mathbf{R}) \rangle &= \{1 - \frac{1}{2}[2n(k) + 1]|\alpha_k|^2\}^2 \\ &\quad + n(k)\alpha_k^*(0)\alpha_k(\mathbf{R}) + \alpha_k(0)[n(k) + 1]\alpha_k^*(\mathbf{R}) \\ &\quad + O(N^{-2}). \end{aligned} \quad (43)$$

From the definition of $\alpha_k(\mathbf{R}_i)$ and the fact that $\omega_k = \omega_{-k}$ and $n(k) = n(-k)$, we obtain

$$\begin{aligned} \langle \chi(n(k), 0) | \chi(n(k), \mathbf{R}) \rangle &= 1 - \{2[2n(k) + 1]|\alpha_k|^2 \sin^2(\mathbf{k} \cdot \mathbf{R}/2)\} \\ &\quad + O(N^{-2}), \end{aligned} \quad (44)$$

so that

$$\begin{aligned} \prod_k \langle \chi(n(k), 0) | \chi(n(k), \mathbf{R}) \rangle &\approx \exp\{-\sum_k 2[2n(k) + 1]|\alpha_k|^2 \sin^2(\mathbf{k} \cdot \mathbf{R}/2)\}, \end{aligned} \quad (45)$$

and finally we obtain the expression for the energy,

$$E(q) = E^0 + \sum_{\mathbf{R}} \mathcal{E}(\mathbf{R}) \exp(i\mathbf{q} \cdot \mathbf{R}) \exp(-\zeta), \quad (46)$$

where

$$\zeta = \sum_k 2[2n(k) + 1]|\alpha_k|^2 \sin^2(\mathbf{k} \cdot \mathbf{R}/2). \quad (47)$$

We see that ζ is positive and increases with the number of magnons excited and therefore with temperature. In order to estimate the magnitude of ζ , consider the case $T = 0^\circ\text{K}$ for which we may set $n(k) = 0$. The sum may be approximated by an integral over a sphere in k space having the same volume as the first Brillouin zone and radius k_m . We use

$$\hbar\omega_k \approx 2ASR^2k^2, \quad (48)$$

and consider a cubic lattice with lattice constant a ; we have then

$$\begin{aligned} \zeta^0 &= \sum_k (4S/N) |J_{12}|^2 \sin^2(\mathbf{k} \cdot \mathbf{a}/2) (\hbar\omega_k)^{-2} \\ &\approx \frac{4S}{\Omega} |J_{12}|^2 \int \frac{\sin^2(\mathbf{k} \cdot \mathbf{a}/2)}{(2ASa^2k^2)^2} d\mathbf{k}, \end{aligned} \quad (49)$$

where

$$\Omega = (2\pi/a)^3 = \frac{4}{3}\pi k_m^3. \quad (50)$$

The result is approximately

$$\zeta^0 = \frac{\pi k_m}{3Sa^2\Omega} \left| \frac{J_{12}}{A} \right|^2. \quad (51)$$

Finally using (43) we obtain:

$$\zeta^0 = \left[12\pi \left(\frac{4\pi}{3} \right)^{1/3} S \right]^{-1} \left| \frac{J_{12}}{A} \right|^2 = \frac{1}{61S} \left| \frac{J_{12}}{A} \right|^2. \quad (52)$$

J_{12} represents an integral connecting functions centered on the same lattice site while A represents a coupling between different neighboring sites so that we can reasonably estimate the ratio $|J_{12}/A|$ to be of the order of 10 or greater. This estimate gives $\zeta^0 = 1.6/S$ (S is measured in units of $\hbar/2$) for a typical ferromagnet at low temperatures.

VII. DISCUSSION AND CONCLUSION

In order to apply this theory in a less schematic fashion to an actual material, it would be necessary to obtain a self-consistent solution to the coupled system of Eqs. (17) and (18). An exponential band narrowing will exist unless the coupling parameter J_{12} vanishes. It is seen from the definition of this quantity, Eq. (25), that J_{12} can vanish only if the electron wavefunction Φ is an eigenfunction of \mathbf{S}_{ez} . Since \mathbf{S}_{ez} does not commute with H_{int} , this situation will not usually occur. There is, however, an exceptional case. If spin-orbit coupling is neglected, and if the ferromagnet is in a state in which no spin deviations are present, then there will be a solution of (17) in which one component of the spinor Φ vanishes and for which $J_{12} = 0$. This corresponds to the usual spin "up" band at $T = 0^\circ\text{K}$. If spin deviations are present the interaction term will not yield a null result. The dynamic interaction never vanishes for an electron in the spin "down" band and therefore it appears that the spin waves may couple more strongly to these electrons and could perhaps

result in a narrower band. When spin-orbit interactions are considered then the situation is somewhat different. Tight-binding solutions for d electrons in a solid with spin-orbit coupling have been discussed by Callaway¹⁴ for body-centered cubic structures and by Lehman¹⁵ for the face-centered cubic case. Their results show that at an arbitrary point in the Brillouin zone the solutions are always two-component spinors. Thus if one includes spin-orbit effects then the dynamic interaction will always be nonvanishing. For the spin "up" band at absolute zero, one would then expect J_{12} to be proportional to the characteristic spin-orbit coupling parameter.

We have seen that the interaction of the individual d electrons with the spin-wave system of a ferromagnet can significantly alter the electron and spin-wave functions. The existence of such effects is not unreasonable since we can expect that the propagation of spin deviations in a ferromagnet will be accompanied by an interaction with the individual electrons. The band-narrowing effect may be altered quantitatively by including anisotropic terms in the spin Hamiltonian with the aid of more sophisticated spin-wave operators and by carrying out the band calculation more carefully. It seems clear that the principal qualitative features should be retained. The basic physical result that d electrons in a ferromagnet interact dynamically with the spin waves does not depend on the nature of the approximations used in treating the spin Hamiltonian.

A similar narrowing of the energy band structure through interaction with the spin waves has been obtained for the antiferromagnet. The results of this investigation will be published at a later time.

¹⁴ J. Callaway, Phys. Rev. **120**, 731 (1960).

¹⁵ G. W. Lehman, Phys. Rev. **116**, 846 (1959).