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Band Structure, Spin Splitting, and Spin-Wave Effective Mass in Nickel†

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We have applied a modified form of the combined interpolation (tight-binding plus pseudopotential) method to the calculation of energy bands in ferromagnetic nickel. A procedure has been developed to enable calculation of the reciprocal spin-wave effective mass in a multiband system in the t-matrix approximation. This has been used in conjunction with the calculated band structure. Matrix elements of the electron interaction are treated as parameters. A by-product of the calculation is an estimate, also in the t-matrix approximation, of the energy difference between majority and minority spin states in the highest d band. Moderately good results for the spin-wave effective mass are obtained for reasonable values of the electron interaction parameters; however, a discrepancy is found in regard to the spin splitting, which appears to be too large.

I. INTRODUCTION

ONE of the outstanding problems in the theory of ferromagnetism in metals is that of calculating the energies of spin waves. In order to do this, one requires not only an energy-band calculation for the particular material, but an adequate theory of spin waves from a many-body point of view which relates the energy of a spin-wave state to the energies of single-particle states described by the band structure. Neither of these items is in completely satisfactory shape, but it is our belief that it is now possible to attempt a quantitative calculation. We have chosen nickel for this purpose, since its band structure is the best understood of the ferromagnetic transition metals. Some previous calculations of energy bands in nickel are listed in the references.[1–14] A fairly substantial amount of experimental information is available concerning the Fermi surface and levels reasonably close to it.[15–20] The degree of agreement between theory and experiment is respectable.

The theory of spin waves in metals is not so firmly established as is the band structure. Most work has been based on the random-phase or equivalent approximations which yield results which are manifestly wrong in certain interesting limits, and on a single-band model Hamiltonian.[21–24] The latter, the so-called Hubbard model[25] is of considerable interest in that it illustrates certain general principles involved in constructing a theory of magnetically ordered systems, but is inadequate in treating real metals of interest which have a complex band structure. An attempt has been made to improve this situation in certain respects in this paper. Other treatments of spin waves in many-band systems, involving different approximations, have been given by Mattis,[26] Thompson,[27] Yamada and Shimizu,[28] and Sokoloff.[29] A previous calculation of spin-wave energies in nickel employs an effective single-band model, and treats the exchange splitting of the d bands as an adjustable parameter.[30]

This work is based on an adaption of Edwards[31] procedure for the calculation of the spin-wave effective mass. This approach has been previously applied to a one-band model ferromagnet.[32] It is supposed that electrons interact only when they are on the same site, or more precisely, we retain only those matrix elements

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of the coulomb interaction between Wannier functions centered on the same lattice site. Terms connecting different bands are included. In the present state of our knowledge it is unfortunately necessary to regard these matrix elements as disposable parameters. The other fundamental approximation of the present calculation is that the renormalized, effective interaction between electrons which enters into the spin-wave calculation, and is essentially the electron self-energy, can be expressed in terms of t-matrix elements. This procedure should be reasonably valid for a low density of particles: In this case we must consider holes. Since the precise nature of the necessary corrections to this approximation are not known at present, the accuracy of the procedure cannot be assessed in a fundamental way.

In order to enable computation of the spin-wave effective mass, we have calculated the energy band structure of ferromagnetic nickel. Our method is closely allied to that of Hodges, Ehrenreich, and Lang,[9] and of Mueller[11] in that it combines a tight-binding treatment of d bands with a pseudopotential procedure appropriate for s-p bands. Our work differs from those calculations primarily in that the tight-binding portion of the effective Hamiltonian is treated more adequately through the inclusion of overlap and three-center integrals previously neglected. However, we do not include spin-orbit coupling.

We obtain as a by-product, the exchange splitting between spin-up and spin-down bands. Essentially, it is this quantity which enters the spin-wave calculation as the effective renormalized interaction which stabilizes the ferromagnetic state. Although this identification is not correct for all particle densities, it does apply in the low-density approximation which is used in this work.

The plan of this paper is as follows. In Sec. II, the theory of spin waves in a many-band ferromagnet is presented. The energy-band calculation on which spin-wave calculation is based is described in Sec. III. The procedures and results of the computation of the spin-wave effective mass are given in Sec. IV. Some final remarks in Sec. V conclude this work.

II. SPIN WAVES IN MANY-BAND SYSTEM

It follows from general considerations that the energy of a long-wavelength spin wave (wave vector $\mathbf{q}$) can be expressed as

$$E=Dq^2. \tag{2.1}$$

We will attempt to calculate D, which is the reciprocal of the spin-wave effective mass, for nickel. Much previous work has been restricted to an idealized case in which only a single energy band is present. This is, conceptually, a poor approximation in the case of nickel, and we wish to obtain an expression for D which can be applied to a many-band situation. In the case of a many-band system, or if matrix elements of the Coulomb interaction between Wannier-function states on different sites are included, other (optical) branches may occur in the spin-wave spectrum[27–29]; however, we will consider only the lowest (acoustic) branch for which (2.1) is valid.

A formally exact expression for D has been derived by Edwards,[31] on which the present work is based. The specific situation we consider is described by the Hamiltonian

$$H=\sum_{l\mathbf{k}\sigma}\epsilon_l(\mathbf{k})c_{l\sigma}{}^\dagger(\mathbf{k})c_{l\sigma}(\mathbf{k}) +\tfrac{1}{2}\sum_{ijln\mu\sigma\sigma'} V_{ijln}c_{i\mu\sigma}{}^\dagger c_{j\mu\sigma'}{}^\dagger c_{n\mu\sigma'}c_{l\mu\sigma}. \tag{2.2}$$

The operators $c_{l\sigma}{}^\dagger(\mathbf{k})$, $c_{l\sigma}(\mathbf{k})$ create or destroy an electron in a Bloch state of wave vector $\mathbf{k}$ and spin σ in band l. The operators $c_{l\mu\sigma}$, etc., refer instead to a Wannier state in band l of spin σ centered on lattice site $\mathbf{R}_\mu$. Thus, the Hamiltonian contains matrix elements of the Coulomb interaction between Wannier functions centered on the same site, but connecting different bands.

The calculation of the coefficient D in (2.1) is somewhat more difficult when the Hamiltonian contains terms coupling bands than in the usual case when these are neglected. In particular, the wave function of the ferromagnetic state is not known exactly in the present situation, whereas for the usual Hubbard Hamiltonian there is no interaction in the ferromagnetic state, and the wave function is a single determinant of Bloch functions. We make the approximation here that the wave function of the ferromagnetic state is still a single determinant. The energy of the exact ferromagnetic state is no longer known exactly, as the electron interaction is now present. It is also assumed that the ferromagnetic state is saturated. No electrons of spin opposite to the majority are present. The restriction to matrix elements between Wannier functions on the same lattice site implies that when one transforms to the Bloch-function basis, the matrix elements of the interaction are independent of wave vector. It is then a straightforward matter to follow the procedure of Edwards and obtain the following expression for D:

$$D=\frac{1}{6n}\sum_{l\mathbf{k}}{}^{(0)}\Big[\nabla^2\epsilon_l(\mathbf{k})-2\sum_{n\mathbf{q}}{}^{(0)}\langle l\mathfrak{k}\uparrow l\mathbf{k}\downarrow|\frac{1}{H-\mathcal{E}-\eta}|n\mathbf{q}\downarrow n\mathfrak{q}\uparrow\rangle \times\nabla_{\mathbf{k}}\epsilon_l(\mathbf{k})\cdot\nabla_{\mathbf{q}}\epsilon_n(\mathbf{q})\Big]. \tag{2.3}$$

The states $|l\mathbf{k}\downarrow,l\mathfrak{k}\uparrow\rangle$ are those in which a single spin has been reversed in band l. We will denote hole states by German letters.

$$|l\mathbf{k}\downarrow l\mathfrak{k}\uparrow\rangle=c_{l\downarrow}{}^\dagger(\mathbf{k})c_{l\uparrow}(\mathfrak{k})|\Psi_f\rangle. \tag{2.4}$$

The state conjugate to $|l\mathbf{k}\downarrow l\mathfrak{k}\uparrow\rangle$ is $\langle l\mathfrak{k}\uparrow l\mathbf{k}\downarrow|$. $\mathcal{E}$ is the energy of the ferromagnetic state $|\Psi_f\rangle$ and n is the number of electrons in the crystal. If N is the number of lattice sites, we have $n/N=\rho$, the particle density. The superscript (0) on a summation indicates that only occupied states are included, and η is a small positive quantity. Following Edwards' procedure, the matrix elements of the resolvent can be analyzed diagrammatically according to the methods of Hugenholtz.[33,34] We employ the Hugenholtz methods here to simplify the expression for D to a practically calculable form.

The main simplification that we introduce is that of considering only diagonal matrix elements of the resolvent, thus introducing factors $\delta_{nl}\delta(\mathbf{k}-\mathbf{q})$ into (2.3). Further, we consider only the contribution of diagonal diagrams (in the sense of Hugenholtz) to these matrix elements. This means the following: The states $|l\mathbf{k}\downarrow l\mathfrak{f}\uparrow\rangle$ defined by (2.4) contain a down-spin electron and an up-spin hole. We consider only those processes in which these particles interact with the medium, for instance, by creating additional up-spin electron-hole pairs; but we do not consider the interaction of these particles with each other: The contribution from nondiagonal diagrams (those in which the initially excited particles do interact) was investigated in the one-band problem, and found to be negligible.[32]

With these approximations we rewrite (2.3) in the form

$$D=\frac{1}{6n}\sum_{l\mathbf{k}}{}^{(0)}\left(\nabla^2\epsilon_l(\mathbf{k})-2\frac{|\nabla\epsilon_l(\mathbf{k})|^2}{U_l(\mathbf{k})}\right), \tag{2.5}$$

where

$$U_l(\mathbf{k})=\langle l\mathfrak{f}\uparrow l\mathbf{k}\downarrow|[1/(H-\mathcal{E})]|l\mathbf{k}\downarrow l\mathfrak{f}\uparrow\rangle^{-1}. \tag{2.6}$$

We consider the evaluation of $U_l(\mathbf{k})$ according to the procedure of Hugenholtz described above. A detailed exposition of the Hugenholtz method is given in Ref. 34. It is convenient, however, to redraw Hugenholtz's diagrams in the Goldstone manner. In this way, one sees that the diagonal diagrams which contribute to the resolvent are just single-particle self-energy diagrams. Each diagram has a down-spin electron line and an up-spin hole line. In the one-band problem usually treated interactions occur only between particles of opposite spin; this means that only the down-spin electron line has a self-energy. This leads to Edwards' result for this case,

$$U(\mathbf{k})=-G_{\mathbf{k}}(\epsilon(\mathbf{k})),$$

G being a function defined by Hugenholtz, which is the negative of the self-energy evaluated at an energy $\epsilon(\mathbf{k})$ above the ground state. In the many-band case, both electron and hole self-energies exist.

According to the procedures of the Hugenholtz method, the matrix elements of the resolvent involving the states $|l\mathbf{k}\downarrow,l\mathfrak{f}\uparrow\rangle$ are to be found by convolution of matrix elements of the resolvent for states containing either a single down-spin electron or a single up-spin hole. The contribution from all diagonal diagrams for the down-spin electron is

$$\langle l\mathbf{k}\downarrow|R(z+\mathcal{E})|l\mathbf{k}\downarrow\rangle=1/[\epsilon_l(\mathbf{k})-z-G_{l\mathbf{k}\downarrow}(z)]. \tag{2.7}$$

In the case of the up-spin hole, we have

$$\langle l\mathfrak{f}\uparrow|R(z+\mathcal{E})|l\mathfrak{f}\uparrow\rangle=1/[-\epsilon_l(\mathfrak{f})-z-G_{l\mathfrak{f}\uparrow}(z)]. \tag{2.8}$$

The matrix element of the resolvent operator between states containing a hole and an electron are found from (2.7) and (2.8) by convolution. We have

$$\langle l\mathfrak{f}\uparrow l\mathbf{k}\downarrow|R(z)|l\mathbf{k}\downarrow l\mathfrak{f}\uparrow\rangle=-\frac{1}{2\pi i}\int_C\langle l\mathbf{k}\downarrow|R(z-\zeta)|l\mathbf{k}\downarrow\rangle \times\langle l\mathfrak{f}\uparrow|R(\mathcal{E}+\zeta)|l\mathfrak{f}\uparrow\rangle d\zeta. \tag{2.9}$$

The contour of integration includes all the singularities of the second factor and none of the first. Finally, we let z approach $\mathcal{E}$. Let ζ_0 be defined as the solution of the equation

$$\zeta_0+\epsilon_l(\mathfrak{f})+G_{l\mathfrak{f}\uparrow}(\zeta_0)=0. \tag{2.10}$$

The final result is

$$\langle l\mathfrak{f}\uparrow l\mathbf{k}\downarrow|R(\mathcal{E})|l\mathbf{k}\downarrow,l\mathfrak{f}\uparrow\rangle =-\frac{1}{G_{l\mathfrak{f}\uparrow}(\zeta_0)+G_{l\mathbf{k}\downarrow}[\epsilon_l(\mathbf{k})+G_{l\mathfrak{f}\uparrow}(\zeta_0)]}. \tag{2.11}$$

As it stands, (2.11) is too complicated to be practical. We will perform the calculation of the G functions only to first order in the particle density. The diagrams which contribute to G are just ordinary self-energy diagrams; however, one must remember that is is a convention of the Hugenholtz method that the G function for electrons has an extra minus sign as compared to the G function for holes, or in other words, that G for electrons is the negative of the usual self-energy, while it is the self-energy for holes.[35] Also, our convention for matrix elements is different from that of Hugenholtz, as may be seen by comparing our interaction, Eq. (2.2) with his (Ref. 34, p. 11). We draw the diagrams in the Goldstone manner, keeping this difference in mind. The series to be considered are just those which contain the smallest possible number of internal hole lines (one). The relevant diagrams are shown in Fig. 1. It should be noted that there are no exchange diagrams for the down-spin electron self-energy, since, according to our hypothesis, there are no down-spin electrons in the ground state. These diagrams are t matrix, or ladder diagrams.

The diagrams of Fig. 1 can be summed following the standard rules. The results can be expressed as follows:

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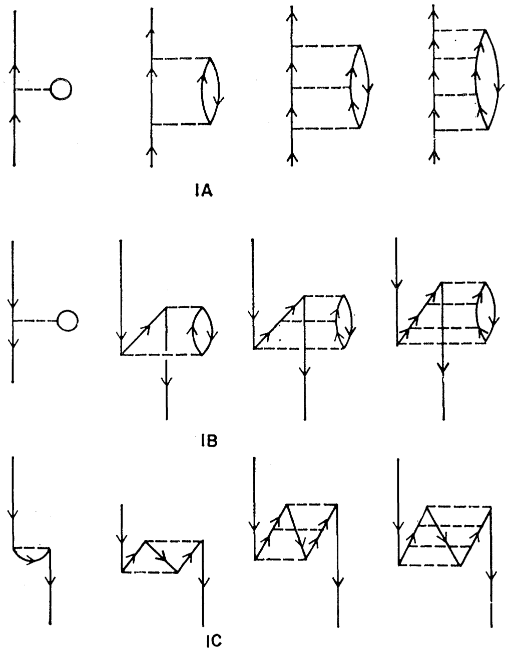

FIG. 1. Goldstone diagrams important in the calculation of the spin-wave effective mass: (a) down-spin electron self-energy; (b) up-spin hole self-energy, direct interaction; (c) exchange diagrams corresponding to those of (b).

(1) Contribution of series of Fig. 1(a) to $G_{l\mathbf{k}\downarrow}(z)$

$$-\frac{1}{N}\sum_{i\mathbf{p}}{}^{(0)}\Bigg[V_{li,li}+\frac{1}{N}\sum_{nj\mathbf{q}}{}' V_{li,jn} \times\frac{1}{z+\epsilon_i(\mathbf{p})-\epsilon_j(\mathbf{q})-\epsilon_n(\mathbf{k}+\mathbf{p}-\mathbf{q})}V_{jn,li}+\cdots\Bigg]$$

$$=-\frac{1}{N}\sum_{i\mathbf{p}}{}^{(0)}t_{li,li}(z,\mathbf{p}).\qquad(2.12)$$

As before, (0) as a superscript on the summation indicates that only occupied states are included, whereas a prime indicates that only unoccupied are included. We have

$$t_{li,li}(z,\mathbf{p})=\sum_{jm}V_{li,jn}F_{jn,li},\qquad(2.13)$$

where

$$(F^{-1})_{jn,li}=\delta_{jl}\delta_{ni}-\frac{1}{N}\sum_{q}{}'\frac{V_{jn,li}}{z+\epsilon_i(\mathbf{p})-\epsilon_j(\mathbf{q})-\epsilon_n(\mathbf{k}+\mathbf{p}-\mathbf{q})}.\qquad(2.14)$$

(2) Contribution of the series of Fig. 1(b) to $G_{l\mathbf{f}\uparrow}(z)$

$$\frac{1}{N}\sum_{i\mathbf{p}}{}^{(0)}\bar{t}_{li,li}(z,\mathbf{p}).\qquad(2.15)$$

Here

$$\bar{t}_{li,li}(z,\mathbf{p})=\sum_{jn}V_{li,jn}\bar{F}_{jn,li},\qquad(2.16)$$

with

$$(\bar{F}^{-1})_{jn,li}=\delta_{jl}\delta_{ni}-\frac{1}{N}\sum_{q}{}'\frac{V_{jn,li}}{2\epsilon_l(\mathbf{k})+z+\epsilon_i(\mathbf{p})-\epsilon_j(\mathbf{q})-\epsilon_n(\mathbf{k}+\mathbf{p}-\mathbf{q})}.\qquad(2.17)$$

(3) Contribution of the series of Fig. 1(c) to $G_{l\mathbf{f}\uparrow}(z)$

$$-\frac{1}{N}\sum_{i\mathbf{p}}{}^{(0)}\bar{t}_{li,il}(z,\mathbf{p}).\qquad(2.18)$$

These formulas are still quite complicated. We make certain additional approximations to reduce them to a usable result. These approximations are consistent with the basic assumption that the electron density is low. We replace ζ_0 by $-\epsilon_l(\mathbf{k})$, neglecting the presence of $G_{l\mathbf{f}\uparrow}$ in (2.10); similarly, set the argument of $G_{l\mathbf{k}\downarrow}$ in (2.11) equal to $\epsilon_l(\mathbf{k})$. Then in the evaluation of the integrals over unoccupied states in the functions F and $\bar{F}$, we neglect the energies and momenta of all occupied states where they occur in the energy denominators. This has been shown to be an adequate approximation at low densities in the one-band problem.[32] The matrices t and $\bar{t}$ are then equal, and are independent of $\mathbf{p}$, so that the final summation over occupied states contributes only a factor of ρ_i, the fractional occupancy of band i ($\rho_i=n_i/n$, where n_i is the number of electrons in band i). Then the combination of Eqs. (2.6), (2.11), (2.12), (2.15), and (2.18) leads to

$$U_l=\textstyle\sum_i t_{li,il}\rho_i.\qquad(2.19)$$

The t matrix elements here are just constants, the matrix F^{-1} now being given by

$$(F^{-1})_{jn,li}=\delta_{jl}\delta_{ni}+\frac{1}{N}\sum_{q}{}'\frac{1}{\epsilon_j(\mathbf{q})+\epsilon_n(\mathbf{q})}V_{jn,li}.\qquad(2.20)$$

The integral includes only those wave vectors $\mathbf{q}$ lying within the Brillouin zone such that the states $j\mathbf{q}$ and $n\mathbf{q}$ are both empty.

Equations (2.19) and (2.20) are the useful results of this section. The modifications necessary to apply them to the actual band structure of nickel will be described in Sec. IV.

Before going on, two comments are relevant. First, we may consider the limit of a very weak potential in which t is replaced by V. This is the Hartree-Fock approximation. Then we have simply

$$U_l\rightarrow\sum V_{li,il}\rho_i.$$

This result is equivalent to that of Yamada and

Shimizu when their Hamiltonian is reduced to ours.[28] Second, we note that U_l is the difference in self-energies of a down-spin electron in band l and an up-spin hole (or electron) in the same band. We may therefore interpret U_l as the exchange splitting of band l. This quantity is of considerable interest in itself. The interpretation we have made is not quite correct in that the $G_{lk\downarrow}$ function which appears in (2.11) is not evaluated at the appropriate energy as is discussed by Edwards in the one-band problem.[31] However, in the present approximation in which the t-matrix elements and F functions are treated as constants, the identification is legitimate.

III. ENERGY-BAND CALCULATION

We will now describe the method and the results of the energy-band calculation which was used in the computation of the exchange splitting and spin-wave effective mass. Our method is closely related to the combination of tight-binding and pseudopotential procedures of Hodges, Ehrenreich, and Lang[9] and Mueller.[11] There are, however, some differences in detail, particularly in regard to the tight-binding portion of the calculation.

It has long been supposed that the d bands in nickel, to the extent that they could be understood in isolation from overlapping s-p bands, could be adequately described by the tight-binding method. However, s-d mixing is not negligible and it is necessary to include some terms into the wave function to represent a somewhat free electron like s-p band. With these requirements in mind it is natural to expand the wave function in a mixed basis set. The elements of this set are (1) tight-binding wave functions for the d levels

$$\Phi_{dn}(\mathbf{k},\mathbf{r}) = 1/N \sum\nolimits_\nu e^{i\mathbf{k}\cdot\mathbf{R}_\nu}\phi_{dn}(\mathbf{r}-\mathbf{R}_\nu)\,, \qquad (3.1)$$

where $n=1, \ldots, 5$ and $\phi_{dn}(\mathbf{r}-\mathbf{R}_\nu)$ is an atomic d wave function centered at $\mathbf{R}_\nu$ and (2) plane waves

$$\Phi(\mathbf{k}+\mathbf{K}_s, r) = (N\Omega)^{-1/2} e^{i(\mathbf{k}+\mathbf{K}_s)\cdot\mathbf{r}}\,, \qquad (3.2)$$

in which $\mathbf{K}_s$ is a reciprocal-lattice vector. Following the usual procedures, four reciprocal-lattice vectors are included:

$$\mathbf{K}_1 = (2\pi/a)(0,0,0)\,, \qquad \mathbf{K}_2 = (2\pi/a)(-2,0,0)\,,$$
$$\mathbf{K}_3 = (2\pi/a)(-1,-1,-1)\,, \qquad \mathbf{K}_4 = (2\pi/a)(-1,-1,1)\,. \qquad (3.3)$$

In the present work, we are concerned with integrals through the Brillouin zone such as are involved in the exchange splitting and the spin-wave effective mass. We do not try to reproduce the Fermi surface in all detail, and therefore do not include spin-orbit coupling in the Hamiltonian. However, we noted that all previous tight-binding plus pseudopotential calculations for nickel have been based on a possibly inadequate tight-binding calculation.[1,2] We have attempted to improve this in several respects. Our objective here is to obtain as good a tight-binding treatment of the d bands alone as possible, and then to add to this at least a reasonable representation of the s-p bands.

First, we note that the basis functions used are not orthonormal, and we have included the overlap matrix S. The energy bands are determined by solving the 9×9 (before consideration of exchange splitting) secular equation

$$\det|H_{ij}-ES_{ij}|=0\,. \qquad (3.4)$$

The matrix elements of H and S between the d states (the 5×5 d-d block) are written as

$$\begin{aligned} H_{nn'} &= \sum\nolimits_\nu e^{i\mathbf{k}\cdot\mathbf{R}_\nu}\int \phi_{dn}^*(\mathbf{r})H\phi_{dn'}(\mathbf{r}-\mathbf{R}_\nu)d^3r\,, \\ S_{nn'} &= \sum\nolimits_\nu e^{i\mathbf{k}\cdot\mathbf{R}_\nu}\int \phi_{dn}^*(\mathbf{r})\phi_{dn'}(\mathbf{r}-\mathbf{R}_\nu)d^3r\,. \end{aligned} \qquad (3.5)$$

In evaluating the matrix elements we considered the integrals including all orbitals up to third nearest neighbors. There are 21 independent integrals involved in $H_{nn'}$ and 9 in $S_{nn'}$ when third neighbors are included. These integrals are denoted (in the notation of Slater and Koster)[36]

$$E_{nn'}(l,m,p) = \int \phi_{dn}^*(\mathbf{r})H\phi_{dn'}[\mathbf{r}-\tfrac{1}{2}a(l\hat{\imath}+m\hat{\jmath}+p\hat{k})]d^3r\,. \qquad (3.6)$$

These integrals were taken from the work of Tyler, Norwood, and Fry.[37] The construction of the crystal potential and the method of evaluation of the integrals is described in detail in that paper; however, we will state briefly some of the essential features here.

The potential consists of a Coulomb and an exchange part. These are determined from an assumed initial charge distribution formed by superposing the electron distribution of free nickel atoms in the configuration d^9s^1. After superposition, a spherical average of the charge density was determined. An exchange potential was constructed from this charge density using the standard Slater $\rho^{1/3}$ procedure. The same exchange potential was used for both majority and minority spin states in nickel. The exchange splitting of the bands into majority and minority spin sub-bands was treated by a procedure like that of Eherenreich and Hodges,[13] as will be described subsequently. The difference in Slater exchange potentials for up- and down-spin states due to the differing occupancies is small, but nonetheless, can be made the basis for a

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[36] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[37] J. M. Tyler, T. E. Norwood, and J. L. Fry, preceding paper, Phys. Rev. **B1**, 297 (1970).

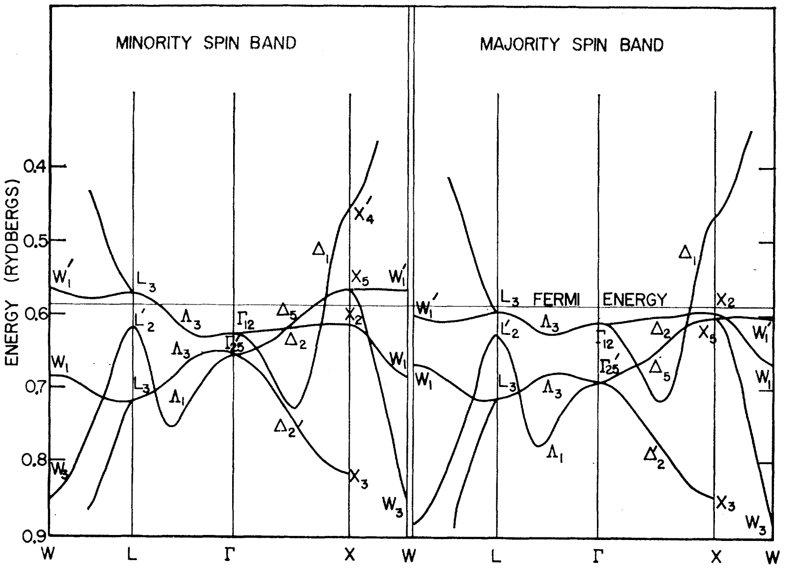

FIG. 2. Band structure of nickel in several directions of high symmetry.

calculation of the exchange splitting of the bands in the ferromagnetic state, as was done by Connolly.[10] Our present procedure can be described as that of grafting an approximate treatment of a short-range electron-electron interaction believed to be responsible for ferromagnetic ordering upon an ordinary band calculation for a paramagnetic system. The relation between the Ehrenreich-Hodges treatment of exchange splittings and that of Connolly remains to be worked out in detail.

The parameters $E_{nn'}$ were computed separately for direct and exchange potentials so that a multiplicative factor of λ could be used to adjust the exchange potential to obtain better agreement if necessary with available experimental information concerning the band structure. We write

$$E_{nn'}(\text{total}) = E_{nn'}(\text{direct}) + \lambda E_{nn'}(\text{exchange}). \quad (3.7)$$

If $\lambda = 1$, the Slater exchange potential[38] occurs, while $\lambda = \frac{2}{3}$ corresponds to the Kohn-Sham-Gaspar[39,40] potential. We found that $\lambda = 0.85$ appears to give the best results. Clementi's wave functions for the $d^8s^2\,{}^3F$ state were used both in the potential and in the evaluation of integrals.[41] Since the potentials used are those of a distribution of spherical charges, crystal field effects may not be represented adequately. For this reason, the parameters $E_{nn'}(l=m=p=0)$ were regarded as adjustable.

The matrix elements of the Hamiltonian between plane waves are written in the form

$$\langle \mathbf{k}+\mathbf{K}_s | H | \mathbf{k}+\mathbf{K}_{s'} \rangle = \alpha (\mathbf{k}+\mathbf{K}_s)^2 \delta_{ss'} + V(\mathbf{K}_s - \mathbf{K}_{s'}). \quad (3.8)$$

The parameters α and $V(\mathbf{K}_s - \mathbf{K}_{s'})$ are regarded as adjustable: that is, as pseudopotential parameters. We inserted symmetrizing factors $F_{\mathbf{K}}(\mathbf{k})$ given by Ehrenreich and Hodges[13] in order to account approximately for the effect of introducing symmetrized linear combinations of plane waves. These factors ensure that proper band degeneracies are obtained at symmetry points of the Brillouin zone.

The matrix elements between d functions and plane waves were treated as follows: Overlap matrix elements S_{ns} are given by

$$S_{ns} = \int \Phi_{dn}^*(\mathbf{k}, r) \Phi(\mathbf{k}+\mathbf{K}_s, r) d^3r. \quad (3.9)$$

These integrals may be expressed in terms of an angular part with the symmetry of dn and a form factor. For example, for the functions of xy symmetry, we have

$$S_{xy,s} = -\left(\frac{60\pi}{\Omega}\right)^{1/2} \frac{(\mathbf{k}+\mathbf{K}_s)_x (\mathbf{k}+\mathbf{K}_s)_y}{|\mathbf{k}+\mathbf{K}_s|^2} G(|\mathbf{k}+\mathbf{K}_s|), \quad (3.10)$$

TABLE I. Parameters used in the energy-band calculation. All parameters are in a.u. (Energies in Ry.)

	Majority spin	Minority spin
α	1.175	1.175
$V(000)$	-1.13	-1.124
$V(111)$	0.28	0.28
$V(200)$	0.38	0.38
B	0.1	0.1
λ	0.85	0.85
$E_{xy,xy}(0,0,0)$	-0.703	-0.671
$E_{3z^2-r^2,3z^2-r^2}(0,0,0)$	-0.7	-0.716

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[38] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[39] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[40] R. Gaspar, Acta Phys. Acad. Sci. Hung. **3**, 263 (1964).

[41] E. Clementi, *Tables of Atomic Functions* (IBM Corp., San Jose, 1965).

where

$$G(k)=\int_0^\infty j_2(kr)R_{3d}(r)r^2dr, \tag{3.11}$$

in which R_{3d} is a normalized radial wave function.

The elements H_{ns} were represented as proportional to S_{ns}

$$H_{ns}=BS_{ns}, \tag{3.12}$$

where B is another adjustable parameter. There are no adjustable parameters in S.

This completes the description of the matrix elements used in Sec. IV for the calculation of exchange splitting and spin-wave effective mass. That calculation used the minority spin bands only. However, we wanted to determine the extent to which observed Fermi-surface properties could be described by the tight-binding and pseudopotential method employed. To this end we made a band calculation for both spin states in ferromagnetic nickel, in which the exchange splitting was treated in the manner somewhat similar to that of Ehrenreich and Hodges.[13]

The s-d exchange term considered by Ehrenreich and Hodges appears in the band calculation as a difference in $V(0,0,0)$ in the two spin states. Similarly, the d-d interaction they use simply gives rise to a difference in the $E_{nn'}(0,0,0)$ for majority and minority spin electrons. There would be a very small effect on $E_{nn'}(R)$ for nonzero values of R, since the d functions on different sites are not orthogonal, but this small correction was neglected. We did not attempt to make a self-consistent calculation of the exchange splitting parameters as did Ehrenreich and Hodges; we merely treated the differences in $V(000)$ and in the $E_{nn'}(000)$ between the two spin states as additional adjustable parameters.

The values of all the adjustable parameters used are listed in Table I. Other (nonadjustable) parameters may be found in the paper of Tyler, Norwood, and Fry.[37]

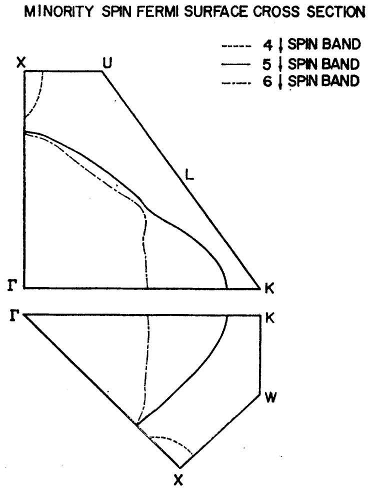

FIG. 3. Fermi-surface contours for minority spin electrons.

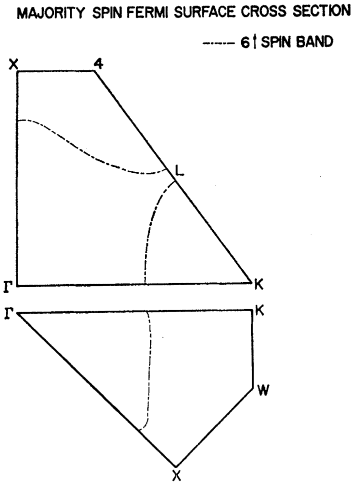

FIG. 4. Fermi-surface contours for majority spin electrons.

The band structure which results from these calculations is shown in Fig. 2. Comparison of these results with other calculations naturally reveals both similarities and differences. We will not explore these in great detail here, but certain general comments are in order. Qualitatively, calculations agree in predicting that the highest d band is nearly flat between X and W, and varies only slowly between W and L. This is, physically, a consequence of the smallness of second-neighbor interactions compared to first-neighbor ones in the tight-binding scheme. If only first-neighbor interactions are included (even if the two-center approximation is not made), in a d band (alone) tight-binding calculation, the energy is independent of wave vector for one band (wave function of symmetry xz) running from X to W. This band connects the two states X_5 and $W_{1'}$. When second-neighbor interactions are included, the band acquires some curvature, but it is so nearly flat that a high peak in the density of states is predicted to occur quite near the top of the d band. This peak in the density of states is responsible for the occurrence of ferromagnetism and for stability of the ferromagnetic state against spin-wave excitation in models employing a t-matrix treatment of strong short-range interactions.[32,42,43] Qualitatively, it is the relative weakness of second-neighbor interactions which makes nickel ferromagnetic.

While the various band calculations are in general agreement about the flatness of the topmost d band, there are differences concerning lower bands. Unfortunately, experiments able to probe the lower d-band structure do not exist. There are, however, quantitative predictions concerning various observed characteristics of the Fermi surface. Calculated Fermi-surface

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[42] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **30**, 275 (1963).
[43] J. Callaway, Phys. Rev. **140**, A618 (1965).

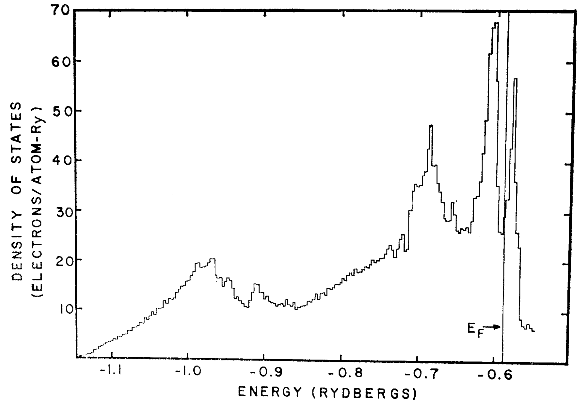

FIG. 5. Density of states for ferromagnetic nickel including both spin directions. The vertical line at E_F indicates the Fermi level.

cross sections are shown for two planes for minority and majority spins in Figs. 3 and 4. A few quantitative results are listed in Table II. The agreement between our results and experiment is not bad; but neither is it outstanding. It has been shown by Ruvalds and Falicov[12] and by Zornberg[14] that inclusion of spin-orbit coupling is necessary to obtain a quantitative accurate description of the Fermi surface.

The arrangement of majority and minority spin bands at the L point is consistent with interpretations of optical measurements.[14,18,19] We note that in the minority spin band, L_3 is above the Fermi energy and $L_{2'}$ below, giving an optical edge of approximately correct energy. In the minority spin band, L_3 is above L_2, and both are below the Fermi energy. A low-energy transition among states near these is possible.

The density of states has been calculated based on a mesh of 24 225 points in 1/48 of the Brillouin zone. It is shown in Fig. 5. Both majority and minority spins are included. The density of states for the different spins are similar except that they contain only a single peak at the top of the band. The presence of two peaks near E_F is due to the spin splitting. From the separation of the peaks in the density of states, it is possible to obtain an over-all estimate of the spin splitting in the most important band. This is determined to be 0.4 eV, in good agreement with the estimate of Zornberg based on analysis of optical-absorption data. However, this estimate of the spin splitting disagrees with one based on the t-matrix procedures described in Secs. II and IV, which give a result twice this, 0.84 eV.

TABLE II. Some characteristics of the Fermi surface.

	Expt. (a.u.)[a]	Calculated (a.u.)
Neck area at L	0.00716	0.00487
Cross-sectional area at X		
in the UXW plane	0.027	0.0206
in the ΓUX plane	0.066	0.047

[a] See Ref. 20.

If the computed density of states is examined at the high-energy end under low resolution, two features would stand out: A high peak slightly below the Fermi energy, followed by a valley around 1 eV below, then followed by a smaller and broader rise, and finally a gradual decrease. Qualitatively, this is just what is observed in the photoemission measurements of Eastman and Krolikowski,[44] although the relation between the so-called optical density of states and the actual one is probably quite indirect.

Because the density of states is large and rapidly varying at the top of the band, it is difficult to obtain the exact magneton number. We obtain 0.635 for this quantity, which is about 13% larger than the value 0.564 deduced from the observed saturation magnetization[45] ($0.616\mu_B$/atom) and the ferromagnetic resonance g factor (2.18).

We conclude that the general features of the band structure are probably given with reasonable accuracy.

IV. SPIN SPLITTING AND SPIN-WAVE EFFECTIVE MASS

In this section, we combine the t-matrix formulas of Sec. II and the band-structure calculation of Sec. III to obtain the spin splitting and the spin-wave effective mass at $T=0$. A previous calculation of the spin-wave energy spectrum by Thompson and Myers in which the exchange splitting is regarded as an adjustable parameter has been noted previously.[30] Other relevant calculations are those of the Harwell group[46,47] concerning the wave number, frequency, and temperature-dependent response function. Their work uses a less realistic band model, ignores interband coupling, and introduces an effective interaction as a parameter, but it covers a much wider range of variables than the present work, which is restricted to a determination of the poles of this function at zero temperature.

Some comments, and some further approximations are necessary before the formulas of Sec. II can be applied to nickel. In nickel, the ferromagnetism is believed to be due to holes in the d band. We ignore the electrons; this is necessary if we are to apply the previous results since the existence of only a single type of carrier was assumed. Attenuation is focused on the minority spin holes occupying the flat band above the Fermi energy in Fig. 2. Possible contribution from majority spin electrons (near L for instance) are ignored. Likewise, we discard the free-electron-like empty minority spin band (Δ_1).

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[44] D. E. Eastman and W. F. Krolikowski, Phys. Rev. Letters **21**, 623 (1968).

[45] H. Danan, A. Herr, and A. J. P. Meyer, J. Appl. Phys. **39**, 669 (1968).

[46] G. Allan, W. M. Lomer, R. D. Lowde, and C. G. Windsor, Phys. Rev. Letters **20**, 933 (1968).

[47] C. G. Windsor, R. D. Lowde, and G. Allan, Phys. Rev. Letters **22**, 849 (1969).

We consider, then, a low-density system of holes. The Hamiltonian, Eq. (2.2), can be transformed in the usual way through the introduction of hole operators $b_l(\mathbf{k})=c_l^\dagger(\mathbf{k})$. In effect this changes the sign of the energy, and we now measure the energy from the highest d-band state, X_5. Additional k-independent terms in the energy are discarded. The spin splitting of the bands is ignored in the calculation of t-matrix elements; the minority spin band being employed for this purpose.

Unfortunately, there are many unknown matrix elements of the potential in the formalism of Sec. II. In order to reduce the number of parameters, we decided to consider only the most important elements of V and to make all those of a given type equal. For all i,j, we put

$$\begin{aligned} V_{ii,ii}&=V_0\,,\\ V_{ij,ij}&=V_d\,,\\ V_{ij,ji}&=J\,. \end{aligned} \tag{4.1}$$

There are then three unknown parameters in the problem. The t-matrix elements can then be easily constructed following methods previously employed.[43,48] The relevant elements are

$$t_{ii,ii}=V_0/(1+g_{ii}V_0) \tag{4.2}$$

and

$$t_{ij,ji}=\frac{J}{(1+g_{ij}V_d)^2-g_{ij}^2J^2}\,,\quad j\neq i \tag{4.3}$$

where

$$g_{ij}=\frac{\Omega}{(2\pi)^3}\int d^3k[\epsilon_j(\mathbf{k})+\epsilon_i(\mathbf{k})]^{-1}.$$

The integrals include those states occupied by electrons (unoccupied by holes) and thus lie below the Fermi energy. They were computed numerically from the band structure. A small correction to $t_{ii,ii}$ of the order $(J/V_0)^2$ has been neglected.[43,48]

It will be observed that the true exchange matrix element J enters in a heavily screened form; nonetheless, its inclusion appears to be important.

The quantity U_l is then evaluated from Eq. (2.19). This is the spin splitting in band l. Note that although the t matrix is symmetric, the spin splitting of different bands is different. This is principally due to unequal occupancy of the bands. Finally, it is necessary to carry out the sum (integral) of Eq. (2.5) over occupied hole states. This was again done numerically, using a grid with approximately 1500 points in 1/48 of the Brillouin zone. The Fermi energy was adjusted slightly in this calculation to give a better magneton number than obtained in Sec. III (the error in this quantity was reduced to about 4%). The results are summarized in Table III for three different and supposedly reasonable choices of the parameters V_0, V_d, and J which have been discussed by Lang and Ehrenreich.[49]

TABLE III. Spin splitting of the highest d band at $T=0$ (U_5) and spin-wave effective mass for three different choices of potential matrix elements.

V_0 (eV)	V_D (eV)	J (eV)	U_5 (eV)	D (Ry a_0^2)
5.0	3.0	1.0	0.84	0.072
7.6	5.0	0.6	0.94	0.044
3.9	3.0	1.0	0.77	0.069
Expt.				0.11±0.01

The results for D quoted are in moderate agreement with experiment. The most recent neutron diffraction results are those of Stringfellow,[50] which give, when extrapolated to $T=0$, $D=0.12$ in atomic units. A number of other measurements have been reviewed by Kaul[51] (who found $D=0.10$ from the temperature dependence of the spontaneous magnetization). The arithmetic average of six measurements listed by Kaul plus the extrapolation of Stringfellow's data yield $D=0.11$. If an error of ±0.01 is allowed, all reported measurements are included.

Our results are somewhat sensitive to the choice of the parameters V_0, V_d, J. For the moderately large V_0 that we believe to be reasonable, the results depend substantially on J. Too small a value of J allows a negative contribution to D from the small number of holes in the second-highest band. However, we believe that the dependence on the details of the band structure is somewhat more significant. This is apparent, both through the dependence of the g_{ij} on the bandwidth, and through the presence of derivatives of the band energy in Eq. (2.5). By altering the parameters which define the band structure, we find that it is possible to produce values of D which exceed the experimental value quoted. This can be done by changing the hybridization parameter B to -0.5. Clearly, in the present situation, little meaning would attach to precise numerical agreement between theory and experiment. We do believe that the results obtained are reasonably good, considering the manifold uncertainties still present in the theory.

A problem arises concerning the value of the spin splitting. The values obtained by the t-matrix calculation are larger by a factor of 2 than given by the Ehrenreich procedure of Sec. III. The present results are not consistent with estimates of this splitting based on optical measurements. On the other hand, if U_5 were reduced to 0.4 eV, the value obtained in Sec. III, the value of D would be reduced to 0.03, far below the experimental value. This discrepancy remains unresolved; however, we note from Ref. 31 that U_l for the spin-wave calculation does not rigorously equal the spin splitting. It is possible that this difference is significant for the actual hole density in nickel.

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[48] J. Callaway and R. K. M. Chow, Phys. Rev. **145**, 412 (1966).

[49] N. D. Lang and H. Ehrenreich, Phys. Rev. **168**, 604 (1968).

[50] M. W. Stringfellow, J. Phys. C1, 950 (1968).

[51] R. D. Kaul, Ph.D. thesis, Case Western Reserve University, 1969 (unpublished).

The present results can also be compared with those of Thompson and Myers.[30] They assumed a band-independent exchange splitting, which was adjusted to yield the experimental value of D and then computed the entire spin-wave spectrum. They found that a band splitting of 0.91 eV was necessary to yield a correct value of D and (at the same time) 0.6 d holes per atom. The same difficulty concerning the spin splitting exists in both calculations.

V. FINAL REMARKS

We have applied a combined tight-binding and pseudopotential scheme to the calculation of the energy band structure of nickel. This procedure is different in some respects from similar procedures employed by others in that the overlap matrix is not assumed to be a unit matrix, and in that an attempt is made to calculate the tight-binding parameters in a more realistic manner. The resulting band structure is used in a t-matrix calculation to obtain the spin splitting of the highest d band and the spin-wave effective mass.

Numerous problems remain. We may not have dealt adequately with the complex system of overlapping bands that exist in nickel. For example, we have considered the bands to be defined strictly in order of increasing energy, and have not considered the complex problems which result from the crossing or the close approach of bands.[52] We have ignored the existence of electronlike portions of the Fermi surface, have neglected bands above the d bands altogether; have treated the holes in nickel as a low-density system, although the validity of this is not established; and have not included spin-orbit coupling or any interaction between electrons on different lattice sites. The critical reader will undoubtedly raise additional objections of his own. However, we recall that the spin-wave reciprocal effective mass is the difference of two quantities; there is no guarantee that one will even obtain $D>0$ (stability against spin-wave excitations). That the results are not unreasonable is perhaps an indication that the most essential features of the problem are understood. We believe that further work in this field will be rewarding.

ACKNOWLEDGMENTS

We acknowledge with thanks helpful discussions with Dr. John Fry and Dr. W. Young.

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[52] J. Callaway and A. J. Hughes, Phys. Rev. **156**, 860 (1967).

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Green's Function Theory of a Heisenberg Ferromagnet with Strong Dipole-Dipole Interactions: Magnetization of $GdCl_3$†

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We have investigated the magnetization as a function of T and H of a spin system with both isotropic Heisenberg exchange and dipole-dipole interactions for $S\geq\frac{1}{2}$ and a hexagonal crystal structure. The Green's functions for such a system, recently derived by Becker, are decoupled in a first-order random-phase approximation. For both Heisenberg-dipole and simple-dipole crystals, we find a lowering of the magnetization below saturation at $T=0$. The Curie-Weiss temperature θ and the ordering temperature T_c are calculated and compared with experimental values on $GdCl_3$. In the limit of zero exchange, we obtain a condition for the type of lattice and shape of domains which make ferromagnetic ordering possible.

I. INTRODUCTION

THE Heisenberg model has been analyzed with the technique of double-time thermodynamic Green's functions (GF) by several authors in various approximations.[1] In this model, the isotropic exchange interaction is assumed to be between nearest magnetic neighbors only. In most real crystals there are, however, long-range interactions such as magnetic dipole-dipole interactions which can influence the thermodynamic properties quite remarkably. An example of such a system is the ferromagnetic insulator $GdCl_3$ where

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[1] For a review of the results see S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum Press, Inc., New York, 1967), p. 247 ff.