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Magnetism in iron and nickel

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The fluctuating local band theory of itinerant electron ferromagnetism in nickel and iron is investigated with the use of first-principles numerical calculations. In this theory the excitations predominantly responsible for the phase transition are fluctuations in the direction of local magnetization. The free energy in the presence of a fluctuation is evaluated numerically in the approximation that this direction changes in time and space slowly enough to justify the use of the static approximation and second-order perturbation theory. The energies and wave functions used to incorporate the band and wave-vector dependence of the relevant interaction matrix elements were obtained by Slater-Koster fits to earlier *ab initio* self-consistent energy bands. Results for nickel and iron are obtained in terms of an effective classical Heisenberg exchange. This is compared with other theoretical calculations and available experimental data. From the numerical results, it is concluded that both quantum effects (the time dependence of the exchange field) and local-field effects are important to account for the transition temperature T_C.

I. INTRODUCTION

The fluctuating band theories[1–6] (FBT) of itinerant ferromagnetism have recently enjoyed considerable success. These theories are finite temperature extensions of band theory which differ markedly from the first such extension, the Stoner-Wohlfarth (SW) theory. They manage to incorporate the successes in the ground state of band theory into a theory of the magnetic phase transition which has some resemblance to the Heisenberg model, although the electrons are never localized.

There are several fluctuating band theories, all of which are much more successful than the Stoner model. The best of the fluctuating band theories account qualitatively for the observed phenomena, and quantitatively get the correct order of magnitude of the energy scale. Thus there are grounds for the conviction that these attempts are on the right track.

However, it must be admitted that nearly all calculations done within the framework of these theories up to now have been based on very crude versions of the band structure. Alternatively, parameters have been chosen phenomenologically. The end result is that the authors of calculations differing from one another by more than a factor of 4 can each be encouraged by their "reasonable" agreement with experiment.

Since the energetics of the band structure underlies the energetics of the elementary excitations in this picture, it is desirable to carry out the basic computations using bands retained to sufficient accuracy that approximations to the bands and the band wave functions are insignificant sources of error. Then it may become possible to assess the other approximations which differ from version to version of the fluctuating band theories.

It was a main aim of the present work to carry out this program for the particular version of the FBT obtained by Korenman, Murray, and Prange[1,2] as well as by Capellmann.[3] In this we believe we have succeeded, although there are some curious numerical differences with other authors which will be discussed later, and the situation is not completely clear cut for nickel.[7]

In the band theory, the interelectron Coulomb interaction is replaced by a single-particle potential and an external exchange field which must be calculated self-consistently by some prescription. We shall, for brevity, explicitly speak only of the exchange field. This is in effect a magnetic field acting only on the electron spin, and has a direction and a magnitude.

In standard SW theory, the exchange field is the same at every site. In the FBT, the exchange field varies from site to site, and an average is taken over its different possible configurations. The form of this average (for the partition function) is as follows[2]:

$$Z=\int D\vec{\mu}\,\exp(-\beta F[\vec{\mu}])\ . \tag{1}$$

Here $\vec{\mu}$ is the exchange field, and F is essentially the free energy of the system of independent electrons in the presence of this field. The exchange field depends on site and, if Eq. (1) is to be made exact, will also depend on an (imaginary) time. If the position dependence in each unit cell is limited to that which can be expanded in a finite number of atomiclike orbitals, the exchange field can depend on orbital quantum number too. The integral then is a sum (functional or path integral) over all configurations of $\vec{\mu}$; that is, over all functions $\vec{\mu}(i\nu\tau)$, where i labels the site, ν the orbit, and τ is the time variable.

At low temperatures, for very large β, the configuration which minimizes $F[\vec{\mu}]$ is most important. This is the constant, SW configuration, while nearby configurations give the spin-wave corrections to that theory. The FBT differ from SW theory by asserting that the temperature dependence is dominated by new configurations which are farther and farther from the SW configuration, rather than by the temperature dependence of the SW configuration itself. Roughly speaking, this says that spin-wave-like excitations are more important than single-particle excitations.

The main approximation common to almost all FBT is to keep only static, τ-independent configurations.[8] One of the main consequences of this approximation is the neglect of certain quantum effects. We find here that the static approximation may have substantial numerical consequences. Secondly, we keep only configurations locally close to the SW configuration in the sense that they are varying slowly in space. We also take as dominant the effect of changes in the direction of the exchange field, rather than its magnitude. (In these approximations we differ from another school[5,6] of FBT which assumes that very large changes of direction are the rule rather than the exception.) We thus have a small parameter which can be used to calculate $F[\vec{\mu}]$ for those configurations we believe to dominate. If the disorder of the configurations is violent, one must rely on alloy theories, adding further uncertainty to the numerical results. Thirdly, we neglect the ν dependence of the exchange field; that is, we neglect local-field effects. Our results give evidence that these effects can be substantial.

Within the framework of these approximations, we have computed the free-energy functional F. This is a first-principles calculation in that we used *ab initio* band structures[9,10] to find the Slater-Koster parameters of a generalized Hubbard Hamiltonian. The energy levels and wave functions of the resulting bands were used to compute F, which takes the form of a classical Heisenberg model. Estimates of T_C are then possible by use of mean-field or spherical-model formulas.

As we discuss below, the static approximation should give too low a transition temperature, and too little short-range order. The neglect of the local-field effects should overestimate the transition temperature (more so for iron than for nickel) and should have little effect on the short-range order. Thus we expect the result of our approximations to be that the ratio of predicted to observed transition temperature in nickel is smaller than that in iron and that there is too little short-range order in both cases. We indeed find the ratio to be about 0.5 for nickel, 1.0 for iron.

Although it is disappointing that the present approximations are inadequate to the extent mentioned, it should be kept in mind that the corrections to them, although difficult to carry out numerically, do not involve new phenomena, but rather the computed value of several constants entering the theory.

II. FORMULATION OF THE THEORY

We generalize Ref. 2 to a multiband system, omitting most of the details. A nine-band (*spd*) short-range exchange Hubbard model,

$$\begin{aligned} H&=\sum t_{i\mu,j\nu}a^{\dagger}_{i\mu\sigma}\,a_{j\nu\sigma}+\sum U_{\mu}n_{i\mu\uparrow}n_{i\mu\downarrow}\\ &=H_0+\sum U_{\mu}n_{i\mu\uparrow}n_{i\mu\downarrow}\ , \end{aligned} \tag{2}$$

is chosen, where $a_{j\nu\sigma}$ annihilates an electron in atomic orbital ν of spin σ on site j, and $n_{j\nu\sigma}$ is the corresponding number operator. The parametrization of the hopping matrix $t_{i\mu,j\nu}$ and the intra-atomic Coulomb interaction U_μ are discussed in Sec. III.

The free energy $F[\vec{\mu}]$ in (1) may be written

$$F[\vec{\mu}]=\sum_{i\nu\tau} U_\nu \vec{\mu}(i\nu\tau)^2+F_0[\vec{\mu}]\ , \tag{3}$$

where F_0 is the free energy of a system of noninteracting electrons with Hamiltonian H_0 in the presence of an exchange field $\vec{\mu}(i\nu\tau)$, namely

$$F_0=-T\ln \mathrm{Tr}\exp_+\left[-\beta\left[H_0-\sum_{i\nu\tau}2U_\nu\vec{\mathrm{M}}(i\nu\tau)\cdot\vec{\mu}(i\nu\tau)\right]\right]\ . \tag{4}$$

The notation indicates that the exponential is time ordered. Here

$$\vec{\mathrm{M}}(i\nu\tau)=\tfrac{1}{2}\exp(\tau H_0)a^\dagger_{i\nu s}\vec{\sigma}_{ss'}a_{i\nu s'}\exp(-\tau H_0)$$

is the magnetization operator and $\vec{\sigma}$ are the Pauli matrices. This form is a generalization of that in Ref. 2, as it contains the orbital quantum numbers. It is still simple because of the choice of diagonal U_ν, i.e., of the formal neglect of interaction between different orbitals. This point will be discussed further in Sec. III.

The configurations of $\vec{\mu}$ which are considered to dominate are locally close to the SW configuration. We thus neglect (or we could treat in Gaussian approximation) the fluctuations in the magnitude $|\vec{\mu}|$. We neglect the dependence of $\vec{\mu}$ on τ (the static approximation) and on ν (neglecting local-field corrections), and we regard the change in the direction of $\vec{\mu}$ as slowly varying. That is, we treat $a_{ij}\equiv|\hat{\mu}_i-\hat{\mu}_j|$ as a small parameter where $\hat{\mu}_i$ is the common direction of the exchange fields on the ith site. This is the approximation of short-range magnetic order.

The free energy is evaluated by utilizing a locally rotated spin coordinate system. In these coordinates the effect of disalignment of the exchange field directions is displayed as a perturbation proportional to a_{ij}. [See Eqs. (10) to (16) of Ref. 2.] The zeroth-order term in a_{ij} is the Stoner free energy (corrected by correlation corrections of the longitudinal and density fluctuations in the random-phase approximation). The first-order term vanishes and the second-order term has the form of a classical Heisenberg energy,

$$F_H=-\sum_{ij}J_{ij}\hat{\mu}_i\cdot\hat{\mu}_j\ . \tag{5}$$

The main numerical result will be the evaluation of the effective Heisenberg exchange J_{ij}. We give the formula for the quantity L, which is essentially the Fourier transform of J,

$$L(\vec{\mathrm{q}})=\sum_{ij}J_{ij}(1-e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}_{ij}})\ . \tag{6}$$

The formula we have evaluated is [see Ref. 2, Eq. (17) and following material] .

$$L(\vec{\mathrm{q}})=-\tfrac{1}{4}\sum_{\nu}U_\nu(M^S_\nu)^2+\tfrac{1}{4}\sum_{n,l,\vec{\mathrm{k}}}\frac{f_{n\uparrow}(\vec{\mathrm{k}})-f_{l\downarrow}(\vec{\mathrm{k}}+\vec{\mathrm{q}})}{E_{n\uparrow}(\vec{\mathrm{k}})-E_{l\downarrow}(\vec{\mathrm{k}}+\vec{\mathrm{q}})}\,|\Delta_{n\uparrow,l\downarrow}(\vec{\mathrm{k}},\vec{\mathrm{q}})|^2\ . \tag{7}$$

Here $f_{n\sigma}(\vec{\mathrm{k}})$ is the Fermi distribution function for energy $E_{n\sigma}(\vec{\mathrm{k}})$, with band index n and wave vector $\vec{\mathrm{k}}$. The matrix elements are

$$\Delta_{n\uparrow,l\downarrow}(\vec{\mathrm{k}},\vec{\mathrm{p}})=\sum_{\nu}C_{n\uparrow\nu}(\vec{\mathrm{k}})C_{l\downarrow\nu}(\vec{\mathrm{k}}+\vec{\mathrm{p}})U_\nu M^S_\nu\ . \tag{8}$$

Here, $C_{n\sigma\nu}(\vec{\mathrm{k}})$ transforms from a Bloch wave composed of atomiclike states to band eigenstates. It is the eigenvector of the effective one electron Stoner Hamiltonian $H_0-\vec{\mu}\cdot\vec{\mathrm{M}}$ with $\vec{\mu}$ constant in the z direction at its minimizing Stoner value M^S_ν. The Stoner magnetization of the νth orbital is

$$M^S_\nu=\sum_{nk\sigma}f_{n\sigma}(\vec{\mathrm{k}})C^*_{n\sigma\nu}(\vec{\mathrm{k}})C_{n\sigma\nu}(\vec{\mathrm{k}})\sigma\ . \tag{9}$$

The Fermi function is approximated by its zero-temperature value. The notation in Eq. (8) is chosen since in the one-band approximation this quantity becomes equal to the exchange splitting, which is independent of momentum in that approximation.

At small q, Eq. (7) reduces to

$$L(q)\sim\Omega A q^2 \,, \tag{10}$$

where Ω is the volume of the unit cell, and A is the Bloch wall stiffness. In the long-wavelength limit this is related to the spin-wave stiffness coefficient D by

$$D=\frac{4\Omega}{n_\uparrow - n_\downarrow}A \,. \tag{11}$$

The Curie temperature can be evaluated from $L(q)$ using the mean-field approximation,

$$kT_C^{\mathrm{MF}}=\frac{2}{3}\frac{1}{N}\sum_q L(\vec{q}) \,, \tag{12}$$

or the Green's-function (spherical model) scheme,[11] which is quite accurate for nearest-neighbor Heisenberg models, at least in the classical limit,

$$kT_C^{\mathrm{GF}}=\frac{2}{3}\left[\frac{1}{N}\sum_q\frac{1}{L(q)}\right]^{-1} . \tag{13}$$

The results are presented in Sec. IV.

III. GROUND-STATE ENERGY BANDS

A. Nature of the fitting procedure

The first step is to determine the parameters of the Hamiltonian H. It has been established that self-consistent energy-band calculations using the same local spin-density functional exchange-correlation potential,[12] but totally different computational schemes, provide a consistent description of the electronic and magnetic properties of the ground state of a solid. The resulting energies and wave functions give a good description of many properties including cohesive energy, lattice constant, bulk modulus, magnetization and form factors, hyperfine field, and Fermi surfaces.[9,10,13,14] A direct fluctuating band generalization of spin-density functional theory has not been written down, however, and even if it were, the resulting formulas would be difficult and expensive to evaluate.

We thus resort to the use of a simple Hamiltonian such as that of Eq. (2). This is, strictly speaking, a pseudo-Hamiltonian. It would be incorrect to find its *exact* solution, as many processes, such as screening, have been "renormalized" away and compensated for by the choice of its parameters.

The pseudo-Hamiltonian is meant to account for the low-energy (a few kT_C or less) states of the system. While this can, in principle, be done in more than one way, we choose a scheme with parameters such that the Hartree-Fock approximation is adequate in the ground state. The Hartree-Fock wave function is not, of course, the correct wave function for the electrons, since many strong correlations exist in the true wave functions which are absent in the Slater determinant. The wave function is rather that of quasiparticles which can be thought of as electrons together with their correlation clouds. However, the energy gained by such strong correlations is so great (several eV, at least) that these correlations must be preserved practically intact in the low-energy states of the system, and can be accounted for by adjusting the constants of the Hamiltonian.

The excited states will be adequately given provided the state concerned is sufficiently close to the ground state, so that the correlations are not greatly disturbed. One main class of excited states which we are considering is that of spin waves of long wavelength, and their nonlinear generalizations. Such spin waves are given in linear theory by the random-phase approximation (RPA), which is well known to be a time-dependent generalization of the Hartree-Fock (HF). Alternatively, the same results are found in the functional integral scheme by considering configurations locally not too different from the Hartree-Fock configuration. Thus we expect that the parameters adjusted to fit the ground-state energy bands will be correct in the calculation of this class of states as well.

We do not choose parameters so that the HF approximation matches the single-particle energies seen in photoemission.[15–19] The states concerned there do not play an important role in the thermodynamics. This class of excitations *does* change the correlation structure of the wave function, so that there are corrections to be made in comparing the energy of the hole with the band-theoretic single-electron level.[20–23] Fitting to the photoemission measurements is possible, but this would be a different scheme, and the resulting pseudo-Hamiltonian would be useful for different purposes. We have therefore decided to use parameters which fit the ground-state bands, as calculated by first-principles theory, and which have been very successful in explaining ground-state properties.

B. Specific fitting procedure

The hopping matrix that appears in Eq. (2) was obtained, therefore, using the semiempirical approach of fitting the spin average of *ab initio* self-consistent energy bands[9,10] derived from the local spin-density functional formalism. Specifically the Slater-Koster linear combination of atomic orbitals (LCAO) method and a basis set consisting of one 4*s*, three 4*p*, and five 3*d* functions was used. This procedure effectively reduced the 75 LCAO basis functions used in the original calculations to nine orthonormal functions. Since we applied the variational theory using LCAO basis functions, not orthogonal to those of the core electrons, it is necessary to include all nine valence and conduction bands in our fitting procedure to keep the higher conduction bands from collapsing. Although these higher conduction bands may not contribute much to the free energy since their *d* admixture and the corresponding matrix elements are small, they may have some effects on the quality of the lower state wave functions which are not checked in the empirical approach employed here. (In effective-mass theory, for example, we know that the curvatures of the energy bands are directly related to the momentum matrix, and thus the wave functions.)

To obtain the parameters we use the least-square-fitting technique of Connolly[24] based on a sampling of 89 (fcc Ni), and 91 (bcc Fe) independent points in $\frac{1}{48}$th of the irreducible Brillouin zone, with energies ordered according to the symmetry of the wave functions to avoid any ambiguity of assigning the energy levels near an accidental degeneracy. Furthermore, states with energies above 1.0 Ry were weighted by a factor of 0.5 to emphasize numerically the importance of the low-lying *d* bands. It is necessary to include a fairly long-range *p-p*, *p-d*, and *s-p* integral since LCAO basis functions are being used to describe the nearly free-electron high-conduction states. The final rms errors are 0.012 and 0.016 Ry for Ni and Fe, respectively. The rms errors are improved (0.007 and 0.012 Ry) if the three higher conduction bands are excluded.

The intra-atomic Coulomb interaction $U_\nu = \Delta_\nu / M_\nu^S$ is taken to be diagonal with two parameters ($\Delta_{t_{2g}}$ and Δ_{e_g}) giving the exchange splittings of the corresponding representations. It is taken to be zero for *s-p* symmetry. The justification for the choice of diagonal screened Coulomb interaction is that very considerable simplification results, while the bands can still be fit well. This choice does leave out explicit reference to the sources of Hund's rule energies. The choice of parameters, however, includes these effects in the ground state, and we are not considering states in which Hund's rule is broken. It may be important to include such terms in an eventual calculation of local-field effects, but it is possible to neglect them in this paper.

The parameters were adjusted to reproduce the overall exchange splitting found in the *ab initio* calculations[9,10] based on the von Barth-Hedin[12] exchange correlation potential. This is a better approximation for Ni, where $E_{n\uparrow}(\vec{k}) - E_{n\downarrow}(\vec{k})$ is almost constant than it is for Fe, where $E_{n\uparrow}(\vec{k}) - E_{n\downarrow}(\vec{k})$ varies substantially over the *d* bands. [$\Delta_{t_{2g}}$ ranges from 1.65 eV (N_2) to 2.11 eV (H'_{25}), and Δ_{e_g} from 1.51 eV (H_{12}) to 2.18 eV (P_{12}).] Additional dispersion arising from the hybridization with *s-p* electrons is included. The parameters chosen are shown in Table I together with the number and magnetic moments of t_{2g}, e_g, and *s-p* electrons. The top panels of Figs. 1 and 2 compare our density of states (solid line) with that of the first-principle results[9,10] (dotted lines). Tetrahedron methods[25] based on 505 (506) points in $\frac{1}{48}$th of the Brillouin zone for Ni (Fe) were used, and Gaussian broadening functions of 0.01 Ry full width at half maximum (FWHM) were included in both *ab initio* and empirical calculations.

The agreement of the empirical bands with the

TABLE I. Exchange splitting (Δ) in Ry, electron density (n), and magnetization (m) for t_{2g}, e_g, and *s-p* electrons.

	Fe			Ni		
	t_{2g}	e_g	*sp*	t_{2g}	e_g	*sp*
Δ (Ry)	0.145	0.160	0.00	0.45	0.45	0.00
n	4.31	2.52	1.17	5.47	3.26	1.27
m	1.10	1.14	−0.09	0.35	0.26	−0.03

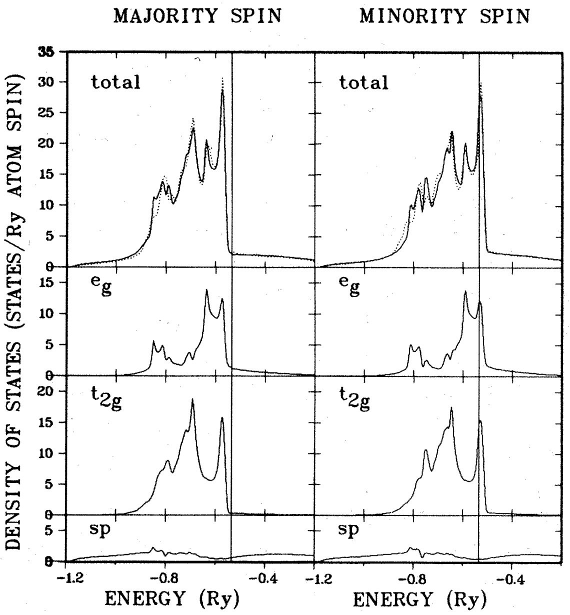

FIG. 1. Total and orbital projected density of states for nickel, including a Gaussian broadening function of 0.1 eV FWHM. The *ab initio* results of Wang and Callaway (Ref. 9) are shown as dotted lines in the top panel for comparison.

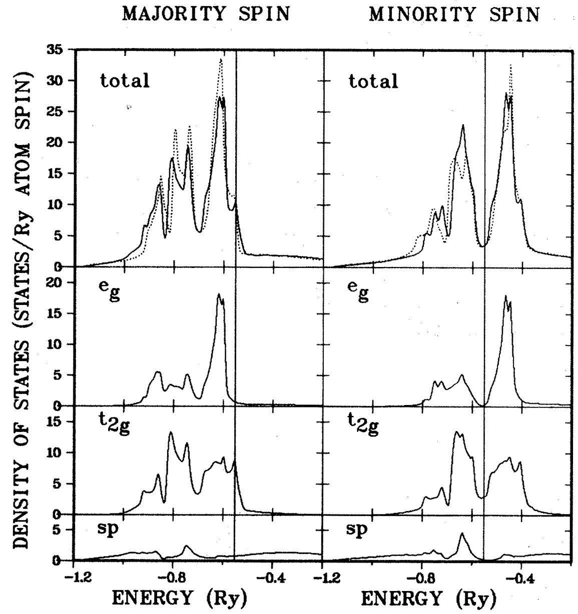

FIG. 2. Total and orbital projected density of states for iron including a Gaussian broadening function of 0.1 eV FWHM. The *ab initio* results of Callaway and Wang (Ref. 10) are shown as dotted lines in the top panel for comparison.

ab initio ones is good with the differences being slightly larger for Fe. The diagonal choice of exchange energy may account for this, since the off-diagonal terms are of importance only if more than one *d* hole is likely to be present on the same atomic site. The remaining panels of Figs. 1 and 2 show the orbital density of states of t_{2g}, e_g, and *s-p* characters. The structure of the *s-p* electrons shown in the bottom panel is due to hybridization with the 3*d* electrons. This is the reason that the number of *s-p* electrons for Ni (1.27) and Fe (1.17) shown in Table I are larger than predicted by Fermi-surface *d*-hole counts.

IV. RESULTS AND DISCUSSION

A. Bloch wall stiffness coefficient

We have calculated $L(q)$ [Eq. (7)] using the tetrahedron method[26] based on 89 (Ni) or 91 (Fe) points in $\frac{1}{48}$th of the Brillouin zone. Results for $\vec{q}$ along the three-principal directions are shown in Figs. 3 and 4 for Ni and Fe, respectively. In the long wavelength limit, the calculated $L(\vec{q})$ for Fe is quadratic with very little direction dependence up to approximately 0.2 a.u., while that of Ni exhibits some anisotropy with maxima along [100] direction and minima along [110] directions. The

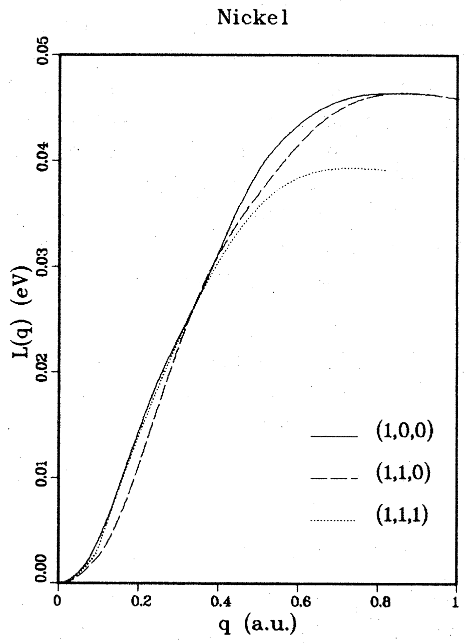

FIG. 3. Fourier transform of the Heisenberg exchange interaction $L(\vec{q})$ [Eq. (6)] for nickel along the three principle directions.

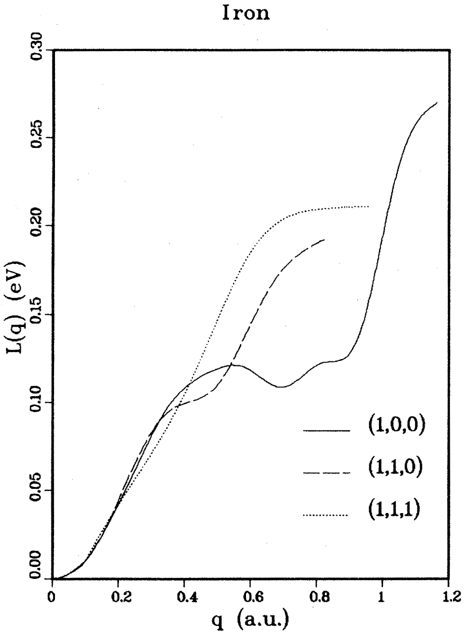

FIG. 4. Fourier transform of the Heisenberg exchange interaction $L(\vec{q})$ [Eq. (6)] for iron along the three principle directions.

angular averaged spin-wave stiffness parameters are shown in Table II where they are compared with first-principles calculations[27] and experimental data.[28] In the case of Ni our results are slightly larger than experiments. In the case of Fe, however, the theoretical value is almost a factor of 2 too large. Such results may appear to be puzzling at first, since it is the ground-state energy bands of Ni rather than Fe that are currently in some doubt. Furthermore, good agreement with the spin-wave spectrum for both Ni and Fe has been reported by Cooke *et al.*[29] using the same approximation as we have made for the exchange and correlation potential. The parameters chosen by these authors are very different from ours for Ni, but quite similar for Fe. Their results, especially for Fe, were not very sensitive to the details of the band structure. The major difference between the two calculations for Fe is that Cooke *et al.* did not neglect local-field effects. This is evidence that such effects can be numerically significant in iron.

Edwards and Rahman[30] have shown that local-field effects, in which the perturbation of the internal structure of the atomic site is taken into account in the RPA, will contribute an additional term to the spin-wave stiffness coefficient. On the basis of previous numerical[31] results, however, they tentatively concluded that such effects are negligible.[32] Cooke *et al.*[29] compute the response (susceptibility) to a varying exchange field which acts on just one atomic orbital. The response is thus a matrix in orbital space which must be suitably diagonalized to find the spin-wave energies. This is a correct way of treating the local-field effects which is facilitated by the choice of a diagonal exchange interaction. In the functional integral method, the local-field effect was omitted when it was assumed that the exchange field $\vec{\mu}_\nu$ is independent of the orbital ν. Constraining the response of the system will raise the estimate of the excitation energy. Qualitatively our calculations, which give larger stiffness than observed for both Ni and Fe, are consistent with the correct sign of the local-field corrections. Numerical calculations for the local-field effects within our formalism appear to be practical and are in progress.

TABLE II. Stiffness coefficients in units of meV Å^2.

	Theory	Experiment
Ni	662,[a] 563[b]	555[c]
Fe	560[a]	330[d]

[a] Present.
[b] Reference 27.
[c] Reference 28(a), neutron scattering measurement at 4.2 K.
[d] Reference 28(b), neutron scattering measurements extrapolated to 0 K.

B. Effective Heisenberg exchange parameters

The Heisenberg exchange parameters J_{ij} evaluated by Fourier transform of $L(q)$ are shown in Table III. In iron J_{ij} changes sign, being fer-

TABLE III. Effective Heisenberg exchange interaction (meV) for Fe and Ni.

Fe		Ni	
R	J_{ij}	R	J_{ij}
(111)	8.9	(110)	1.93
(200)	9.7	(200)	0.38
(220)	−0.5	(211)	0.38
(311)	8.0	(220)	0.30
(222)	−2.3	(310)	−0.04
(400)	0.9	(222)	−0.05
(331)	0.3	(321)	0.04
(420)	0.3	(400)	0.04
(422)	−0.3	(330)	0.02
(333)	3.1	(411)	0.02

romagnetic between nearest neighbors but antiferromagnetic at longer range. The ferromagnetic ground state is stable. This is not a trivial result, as the Bloch wall stiffness can easily turn out to be negative, especially if *s-p* bands are omitted.[33] The competition between short-range ferromagnetism and long-range antiferromagnetism can lead to enhanced short-range order, as nearby spins are kept aligned when long-range disorder has become favorable. For nickel, however, J_{ij} is a monotonically decreasing function of the atomic separation. Thus our calculations, based on the classical Heisenberg model, predict somewhat more short-range magnetic order (SRMO) in iron than in nickel, but in both cases the scale is insufficient to fit the numbers derived from the neutron and specific-heat data.

Another interesting difference between nickel and iron is the fact that J_{ij}, in the case of nickel, is of rather short range, being essentially zero beyond the fourth-nearest neighbors, while in the case of iron, J_{ij} remains appreciable over a very long range along the [111] direction. Some of these differences can be seen from the structure in $L(\vec{q})$ for Fe in Fig. 4. This structure is due to the sudden cutoff of $f_n(\vec{k})$ and/or $f_l(\vec{k}+\vec{q})$ [see Eq. (7)], over a large region of the Brillouin zone which occurs if the Fermi surfaces are flat and perpendicular to $\vec{q}$. As can be seen from Fig. 2, states near the Fermi energy are predominantly of t_{2g} character in iron. Therefore, the J_{ij}, which is the Fourier transform of $L(\vec{q})$, converges very slowly along the nearest-neighbor [111] direction where the t_{2g} *d* orbitals point.

There have been several previous attempts to evaluate J_{ij} for iron. Including only the nearest-neighbor interactions, Weiss[34] obtained $J_{01} \sim 5$ meV which is of the same order of magnitude as ours. More recently, several calculations[33,35] have used the recursion method for a large cluster of atoms whose spins are arranged to extract information about the exchange interaction. Owing to the size of the cluster, most of these calculations were limited to the five *d*-band tight-binding model, neglecting completely the *sp-d* hybridization. The calculations, however, are not limited to the short-range order approximation assumed here. The resulting J_{ij}, up to fifth neighbors, are a factor of 3 to 7 larger than ours depending on the particular model used to simulate the Heisenberg exchange interactions. (The published constants give negative stiffness values, and would predict a nonferromagnetic ground state.[33] This is an artifact of the analysis which was used to obtain real space J_{ij} from configuration energies however, as the basic calculations show the ground state to be ferromagnetic. A re-analysis has recently appeared.[35]) Although we differ by a considerable factor on the magnitude of the exchange constants, we do agree on the long range in the [111] direction and on the competition between ferromagnetism and antiferromagnetism.

C. Curie temperature

Several distinct calculations[3,5,33,35] based on the fluctuating band theory have been used recently to estimate the Curie temperature T_C in iron and nickel. In most of these estimates a single-site approximation (corresponding to the mean-field theory in the Heisenberg model or the coherent-potential approximation) has been made. A characteristic of such an approximation is that spin configurations with wave numbers in the outer part of the Brillouin zone dominate the determination of T_C, due to the greater volume of momentum space there. The quoted value of T_C in these theories contains corrections, different in each case for quantum, alloying, and/or nonlinear effects, but in several cases, the mean-field estimate T_C^{MF} [i.e., Eqs. (7) and (12), but with the bands used by the authors in question] can be extracted from the published results. This number depends only on the band structure, and a comparison can thus afford an assessment of the importance of this aspect of the problem.

Hubbard[5] estimated the cost in energy to change the exchange field at a single site while keeping the fields at other sites fixed at their zero-temperature value. A special case is the energy cost upon changing only the direction of the exchange field by a small angle ϕ with all other fields. It is straightforward to show that this energy is $kT_C^{\mathrm{MF}}\phi^2/6$. Capellman[3] derived, using a different approach, a classical Heisenberg model with exchange coupling equivalent to ours. These two authors use what amounts to a five-independent-band approximation, with everything assumed diagonal in the band index. Once that approximation is made, only the density of states (DOS) appears in the formula. Hubbard takes each independent DOS to be one-fifth the total *d* band DOS. Capellmann takes the e_g DOS twice and the t_{2g} DOS three times. These approximations are denoted T_C^{MF1} and T_C^{MF2}, respectively.

The Cambridge group[33,35] considers various spin arrangements of a large iron cluster. They employ a tight-binding model with five d orbitals and neglect in most cases, the sp bands. Among the configurations considered by Lin-Chung and Holden is the one calculated by Hubbard. These authors use a novel calculational scheme based on the continued fraction recursion method. This method includes wave-function effects.

As can be ssen from Table IV, there is a factor of 4 difference between the largest and smallest result. We emphasize that this arises only from differences in approximations to the band energies and wave functions (and, conceivably, from the numerical treatment employed).

To test the sensitivity of the independent-band approximation we have repeated the calculations using our projected DOS shown in Figs. 1 and 2. Letting Δ be constant in Eq. (7), which gives a rigid exchange splitting, doing the sum over q, $T_C^{\mathrm{MF}i}$ $(i=1,2)$ can be written as follows:

$$kT_C^{\mathrm{MF}i}=-\frac{\Delta}{6}\sum_{\nu}\int_{-\infty}^{E_F}dx\int_{E_F}^{\infty}dy\left[\frac{\Delta+x-y}{x-y}\rho_{\uparrow\nu}(x)\rho_{\downarrow\nu}(y)+\frac{\Delta-x+y}{x-y}\rho_{\downarrow\nu}(x)\rho_{\uparrow\nu}(y)\right], \tag{14}$$

where $\rho_{\nu\sigma}(E)$ is the (orbital projected) DOS for spin σ and E_F is the Fermi energy. This equation has been written to have a singularity only at $x=y=E_F$. It is equivalent to Capellmann's[3] expression. The result obtained using the d DOS for all ν $(i=1)$ or t_{2g} and e_g DOS $(i=2)$ are shown in Table IV. For this calculation, the combined approximations of neglecting s-p states and using an effective one-band model has an effect of order 20%.

One problem is that the number of d electrons (n_d) is ambiguous if sp states are neglected. Capellmann has found that T_C for iron [including a factor $S(S+1)$ for quantum corrections (see Sec. IV D)] ranges from 800 K $(n_d=6.8)$ to 1300 K $(n_d=7.2)$. Both Hubbard and Lin-Chung and Holden choose n_d to be 7.36 electrons for iron while our calculation which allowed sp-d hybridization yielded 6.8 d electrons.

TABLE IV. Curie temperature for Ni and Fe evaluated by the Green's-function scheme (T_C^{GF}) or mean-field approximation (T_C^{MF}). Additional approximations to the matrix element (see text) are denoted by T_C^{MF1} (using d electrons density of states) and T_C^{MF2} (using t_{2g} and e_g density of states).

	Fe	Ni
T_C^{MF}	1220[a]	320[a]
	1900[b]	
T_C^{MF1}	1420[a]	290[a]
	1200[c]	
T_C^{MF2}	1250[a]	280[a]
	550[d]	200[d]
T_C^{GF}	1051[a]	290[a]
T_C^{expt}	1043	631

[a] Present.
[b] Reference 35.
[c] Reference 5.
[d] Reference 3.

In the case of nickel, the exchange splitting is an important parameter. Capellmann noted a linear dependence of T_C on Δ in the region between 0.2 and 0.5 eV. We have not so far tested the sensitivity of our results to a change of Δ. Our Bloch wall stiffness, however, is not much larger than that of Cooke *et al.*[29] who used a much smaller value than we did.

The factor of 2 disagreement between our results and those of Refs. 3 and 35 is not readily explained. The latter authors used a novel method, which has not been so thoroughly tested and which could conceivably be subject to unsuspected errors. We are inclined to believe that the technique is sound and that the neglect of s-p bands has a large effect which is compensated by the one-band approximation used in Ref. 5. The relatively low results of Ref. 3 must then arise from a surprising sensitivity of the calculations to details of the assumed density of states. Whatever the case, the common wisdom that it is adequate at the 20% accuracy level to make considerable simplifications in band calculations of this type is clearly suspect.

Although the mean-field approximation facilitates comparison of different band theoretical approximations, a superior approximation is given by the Green's-function (or spherical model) method, and results in Eq. (13). A major improvement is that the Green's-function formula properly accounts for the importance of the long wavelength configurations. The relatively modest lowering of the value of T_C as compared with the mean-field result indicates that our results do not predict much short-range order. The results are given in Table IV. Although the theoretical value for iron agrees well with experiment, it should be recalled that our theoretical value of A for iron was almost twice as large as found experimentally. A calculation which gives an effective Heisenberg Hamiltonian having the observed value of A will thus lower the predicted T_C substantially. This will be true if the Green's-function formula is used, even if the short wavelength energy spectrum is not changed appreciably. It is then clear that the correct (including local-field corrections) classical Heisenberg model based on the static approximation significantly underestimates the transition temperature for both nickel and iron.

D. Quantum effects

We have arrived at a classical Heisenberg model as an approximation to the energies of spin configurations which appear in the functional integral representation of the partition function. The time dependence of the fluctuations arises from the need to account for the failure of the components of spin operators $\vec{\mathrm{M}}(i\nu\tau)$ to commute with one another and with H_0. The static approximation is classical insofar as it neglects these commutators.

The traditional estimate of the importance of quantum effects on T_C comes from the single-site approximation, and results in an enhancement of T_C by a factor $S(S+1)/S^2$, a factor usually estimated as about 2 for Fe and 3 for Ni. This is the quantum correction used by Capellmann[3] and others.[36]

It is clear, however, that the correction is wave-number dependent, as may be seen from spin-wave theory. First, there is no factor of this type, in the calculation of the spin-wave constant D or A. Second, provided the temperature satisfies $kT >> E_q$, where E_q is the quantum of energy (given approximately by Dq^2), then the effects of thermal excitation of the spin wave may be treated classically. Although the static approximation is sometimes justified as a high-temperature approximation, this is only correct if there is a gap in the important excitations such that some of the excitations are highly excited thermally but all others are negligibly excited. We have every reason to believe, however, that magnetic excitations enjoying appreciable phase space extend continuously up to at least twice T_C in iron and nickel. This is in contrast to the insulating ferromagnets which have a maximum magnon energy comparable to T_C.

In spin-wave theory, it is clear that the classical approximation greatly overestimates the degree to which the short wavelength configurations near the zone boundaries are excited, thus decreasing the magnetization much more rapidly with temperature, lowering the predicted T_C and leading to less short-range order than observed. Unfortunately, the spin-wave theory is a linearized theory, and no method presently known is able to assign definite quanta of energy to nonlinearly excited configurations.

Another effect of the static approximation is to render uncertain the basic energy calculations in the short wavelength region. These calculations have neglected terms with nonvanishing thermal frequencies $\omega_n = \pi kT(2n+1)$ in energy denominators on the basis that they were practically independent of wave number and contributed only to J_{ii}. However, in the short wavelength region, the difference in band energies is comparable with the thermal energy and such terms are not obviously negligible. In fact, it is known that in the short wavelength region corresponding to the Stoner continuum, there is a rapid decay of spin excitations into particle-hole excitations.

The estimate of the energies at short wavelengths, corresponding to the Stoner continuum, is thus uncertain for a number of reasons. In addition to the ones just mentioned, there is the question of the validity of the effective Hamiltonian in this energy range, as well as the question of whether vertex corrections are needed when the correlation of the particle-hole pairs is reduced. Even given the energies correctly, it will be difficult to take into account the quantum effects in doing the statistical mechanics.

V. SUMMARY

We have attempted to calculate spin-configuration energies using approximations to the band structure which are not a main source of error. Although this procedure ends up within sight of a final theory, there are still significant corrections to be made, and improved formulas must be employed. One relatively simple correction is that of local-field effects.

A much deeper problem is that of dealing with the failure of the static approximation. This problem manifests itself as that of calculating, counting and quantizing the energies of short wavelength excitations. (In other versions of the theory,[6] which deal only with Ising-like spin configurations, even the long wavelength spin-wave excitations can only be obtained by abandoning the static approximation.) This kind of excitation cannot be observed directly and is of interest only through indirect and average effects on a few quantities like T_C, the Curie constant, and the degree of short-range order.

Several papers have recently appeared which conclude that there is little short-range magnetic order (above T_C) in iron[36–39] or even in nickel.[39] The basis for this conclusion in all cases is that in a Heisenberg model (treated in an approximation in which quantum corrections are independent of q), the spin-correlation function $C(\vec{q})=\langle S_i(\vec{q}) \times S_i(-\vec{q})\rangle$ falls off smoothly with increasing q. The integral of C over $\vec{q}$ is fixed at a (large) value [approximately $S(S+1)/3$ as in a pure Heisenberg model]. The value $C(0)/T$ gives the susceptibility $\chi(T)$ (and thus the Curie constant can be found). In this model, the greater the degree of short-range order, the greater is the peaking of $C(q)$ near $q=0$, and because of the integral condition, the greater is $C(0)$ and thus the Curie constant. Numerically, it is then difficult if not impossible for the theory to achieve a degree of short-range order sufficient to explain the experimental data on neutron scattering,[40] specific heat,[41,42] and magnetoelasticity[42] at the same time predicting that the magnitude of the Curie constant is as small as is observed. Since fluctuating band theories in the static approximation give an effective Heisenberg model, these theories too are defective in this regard, as we have found in this paper.

One therefore has the choice of maintaining that the FBT in the static approximation is accurate in its prediction of short-range order (thus implying that there is no short-range order) or of accepting that the experimental data require short-range order and thus recognizing the need to improve the implementation of the FBT by including quantum corrections.

The leading alternative in the FBT which has no short-range order is the generalization of the local moment theory.[5,6] Hubbard[37] has emphasized that this form of the theory cannot be expected to apply to nickel, which would need a different theory than iron. Thus, abandoning short-range order would require new explanations of those experimental data which now are easily explained on the basis of short-range order,[1,40–42] and these explanations would presumably be quite different for iron than for nickel. Our choice is to accept the experimental data as requiring short-range order and to search for ways to improve the theory which will enable the degree of short-range order to be calculated from first principles. Some ways in which the extension might be carried out are discussed in Ref. 43.

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