

Character of the Ferromagnetic Transition in Fe and Ni

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The magnetism of Fe and Ni is investigated by a cluster theory with two novel features: (i) The coupling of magnetic moments formed by clusters (described by a local band theory) is determined, thus incorporating short-range order as well as collective modes. (ii) The clusters are coupled by source and sink terms describing transport processes. The results indicate that Fe is closer to a local moment system, whereas Ni seems to be a prototype for a local band theory.

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The existence of spin waves above T_c in Fe and Ni,¹⁻³ suggesting a physical model that is neither strictly localized nor fully itinerant, led to the development of the local band theory.⁴⁻⁷ The basic idea of this theory is the assumption of a magnetically correlated region that is large enough to define ferromagnetic bands. This is equivalent to dividing the degrees of freedom into two groups: (i) The degrees of freedom pertaining to the local band, i.e., one-particle excitations and random-phase-approximation (RPA) spin waves.⁸ (ii) The degrees of freedom corresponding to long-wavelength excitations formed by the slow change of the direction of the local magnetization from site to site.

In principle one would like to solve the equations for these two sets of degrees of freedom and their mutual interaction self-consistently. This problem has not yet been solved. Korenman and Prange in their first three papers,⁴ as well as in a more recent paper on photoemission,⁹ calculated the renormalization of the local bands (assumed to be of Stoner form) and of the spin-wave stiffness due to the long-wavelength excitations [described by Korenman and Prange⁹ by the spectral function $D(k, \omega)$]. But they did not—nor did anyone else—determine the dynamics of the second set of degrees of freedom; i.e., the spectral function $D(k, \omega)$ remained undetermined so that no thermodynamic quantities like T_c could be determined. All previous thermodynamic calculations (IV and V of Refs. 4-6 and 10-12) are based on effective Heisenberg systems with *atomic* local moments. In the following I treat the ferromagnetic metal as an assemblage of clusters or *extended* local moments whose coupling is determined. This has never been calculated before. An extended moment also guarantees that the energy of the coupling between the moments is much smaller than the energy required to form the moment in the first place

(otherwise the notion of a moment of fixed magnitude does not make sense).

In implementing this idea the Hubbard model served as a starting point:

$$H = \sum_{ij\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}.$$

Here the sites $\{i\}$ form a lattice, σ takes two values [down (\downarrow) or up (\uparrow)], the t_{ij} , which form the hopping matrix, are usually taken as a constant t when i and j are nearest neighbors and zero otherwise, $c_{i\sigma}^\dagger$ and $c_{i\sigma}$ are creation and annihilation operators of a local state at the site i with spin σ , and $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. In the next step one restricts this Hamiltonian to a cluster:

$$H^{\text{cl}} = \sum_{ij\sigma}^{\text{cl}} t c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i^{\text{cl}} n_{i\uparrow} n_{i\downarrow} + t \sum_{ij\sigma}^{\text{bd}} c_{i\sigma}^\dagger c_{j\sigma}.$$

In this equation "cl" denotes a sum extended only over lattice sites within the cluster, whereas "bd" denotes a sum over lattice sites i and j where only one of these sites is situated within the cluster. The first two terms describe the local band. I assume here, as Korenman and Prange⁴ did, that they can be approximated by Stonerlike ferromagnetic bands which we take from experiments. This is of course only a substitute for a detailed calculation which is in progress. Thus we replace $\sum_{ij\sigma}^{\text{cl}} t c_{i\sigma}^\dagger c_{j\sigma} + \sum_{ij\sigma}^{\text{cl}} n_{i\uparrow} n_{i\downarrow}$ by $\sum_{k\sigma} \epsilon_{k\sigma} n_{k\sigma}$, where $\epsilon_{k\sigma}$ is taken to be a bulk ferromagnetic band (cf. later discussion) independent of h , whereas the dependence on h is due to restricting the values of the momentum components k_i to multiples of $2\pi/\Delta h$, where Δ is the distance to the nearest neighbor and h^3 is the number of atoms in the (cubic) cluster. The last term describes the interaction of the cluster with its environment. In contrast to usual cluster theories this interaction is not a coupling by exchange fields. The potential $U n_{i\uparrow} n_{i\downarrow}$ is strictly local and does not couple dif-

ferent lattice sites. The information transfer between the cluster and its environment is accomplished by the moving electrons. Therefore instead of physical magnetic fields I introduce source and sink terms describing the flow of electrons into and out of the cluster. This method has already been used by Caron and Pratt¹³ for a "cluster" consisting of one site only in order to describe the metal-insulator transition. Introducing source and sink terms means replacing those creation and annihilation operators referring to lattice sites outside the cluster by expectation values $\gamma_{i\sigma} = \langle c_{i\sigma} \rangle$ and $\bar{\gamma}_{i\sigma} = \langle c_{i\sigma}^\dagger \rangle$. The cluster Hamiltonian then has the following form:

$$H^{cl} = \sum_{k\sigma} (\epsilon_{k\sigma} - \mu) n_{k\sigma} + \sum_{k\sigma} (\gamma_{k\sigma} c_{k\sigma}^\dagger + \bar{\gamma}_{k\sigma} c_{k\sigma}),$$

$$\gamma_{k\sigma} = \sum_i^{\text{bd}} \gamma_{i\sigma} \exp(ikR_i) / h^{3/2},$$

where R_i is the position of the lattice site i . Here the chemical potential μ had to be introduced because the Hamiltonian no longer conserves particle number.

For a magnetically homogeneous system one can derive a self-consistent equation in a way that is similar to the usual cluster theories. In principle one could calculate $\gamma_{i\sigma} = \langle c_{i\sigma} \rangle_{H^{cl}} = f(\{\gamma_{i\sigma}\})$ and solve for the $\gamma_{i\sigma}$ (the $\langle c_{i\sigma} \rangle$ are $\neq 0$ because the Hamiltonian does not conserve particle number). But as we shall see it is easier to make use of translational invariance. These expectation values are related to the first-order perturbation term in a perturbation expansion around the atomic or local limit of the Hubbard model:

$$H = H_0 + V;$$

$$H_0 = U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad V = \sum_{ij\sigma} t c_{i\sigma}^\dagger c_{j\sigma}.$$

In the half-filled band case the ground state of H_0 contains one particle per atom. Hence it is non-degenerate and there is no first-order term. The second-order term describes antiferromagnetically coupled atoms, i.e., atoms coupled by an ef-

fective exchange field with a coupling constant $J \sim t^2/U$, where this coupling is entirely due to virtual transitions. A corresponding effective Hamiltonian^{14,15} obtained by a sort of Schrieffer-Wolff technique¹⁶ does not contain any mixing terms $c_{i\sigma}^\dagger c_{j\sigma}$. The general case ($n \neq 1$) is quite different: The ground state is macroscopically degenerate and perturbation theory is not possible with (antisymmetrized) product states of the form $\prod_i |\varphi_i\rangle$ (i denoting lattice sites and φ_i solutions of $U n_{i\uparrow} n_{i\downarrow} |\varphi_i\rangle = E |\varphi_i\rangle$) because of vanishing energy denominators. This means zero-energy excitations are possible: Namely electrons may hop from site to site (actually it is a somewhat restricted hopping¹⁵) without violating energy conservation, i.e., these are *real* transitions and constitute an electron *current* or transport. To describe this it would be necessary to change to new basis functions that are superpositions of different atoms to eliminate any coupling by V between states of the same energy. Then the first-order term will contribute, as a result of these real transitions between different atoms.

These real transitions or currents are partially taken into account in the above approximation by describing the current *between* clusters by source and sink terms. There is an additional problem: In the original Hamiltonian the terms $c_{i\sigma}^\dagger c_{j\sigma}$ and $c_{i'\sigma}^\dagger c_{j'\sigma}$ commute for different boundary lattice sites, i.e., the electrons leave and join the cluster *independently*. After the approximation the $\gamma_{i\sigma}$'s are numbers instead of fermion operators, destroying this independence. The expression $\sum_i^{\text{bd}} (\gamma_{i\sigma} c_{i\sigma}^\dagger + \bar{\gamma}_{i\sigma} c_{i\sigma})$ can be rewritten as $N(c_{\gamma\sigma}^\dagger + c_{\gamma\sigma})$, where the $c_{\gamma\sigma}$ denote a fermion operator with $N = \sum_i |\gamma_{i\sigma}|^2$, $c_{\gamma\sigma} = N^{-1} \sum_i^{\text{bd}} \bar{\gamma}_{i\sigma} c_{i\sigma}$ describing electrons leaving or joining the cluster coherently.¹⁷ This is due to the fixing of the phases of the $\gamma_{i\sigma}$ by taking expectation values and is similar to broken gauge invariance in superfluidity (e.g., Ref. 18). The remedy consists of two steps: averaging over the phases ψ_i in $\gamma_{i\sigma} = \gamma_\sigma \exp(i\psi_i)$ and restoring the correct commutation rules. This is most easily done in the k representation:

$$\langle |\gamma_{k\sigma}|^2 \rangle = \gamma_\sigma^2 \sum_{ij}^{\text{bd}} \langle \exp(i\psi_i) \exp(ikR_i) \exp(-ikR_j) \exp(-i\psi_j) \rangle / h^2 = \gamma_\sigma^2 \sum_{ij}^{\text{bd}} \langle \exp(i\varphi_i - i\varphi_j) \rangle / h^3$$

$$= \gamma_\sigma^2 \sum_i^{\text{bd}} 1/h^3 = \gamma_\sigma^2 / h.$$

This averaging leads to the following cluster Hamiltonian:

$$H^{cl} = \sum_{k\sigma} (\epsilon_{k\sigma} - \mu) n_{k\sigma} + \sum_{k\sigma} \gamma_\sigma (c_{k\sigma}^\dagger + c_{k\sigma}) / \sqrt{h} = \sum_k H_k.$$

Restoring correct commutation rules means all H_k can be diagonalized separately. The Hamiltonian can now be solved with the result

$$E_{k\sigma} = \frac{1}{2}(\epsilon_{k\sigma} - \mu) - \frac{1}{2}[(\epsilon_{k\sigma} - \mu)^2 + \gamma_{\sigma}^2/\hbar]^{1/2}.$$

Here I always chose the solution which corre-

$$\begin{aligned} t \langle c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \rangle &= \langle \gamma_{i\sigma} c_{j\sigma} + \bar{\gamma}_{i\sigma} c_{j\sigma}^\dagger \rangle = 2\gamma_{\sigma}^2/t \\ \Rightarrow |\gamma_{\sigma}|^2 &= \frac{1}{2}t^2 \langle c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \rangle = \frac{1}{2}t^2 N^{-1} \sum_{kk'} \exp(ikR_i - ik'R_j) \langle c_{k\sigma}^\dagger c_{k'\sigma} \rangle + \text{H.c.} \\ &= \frac{1}{2}t^2 N^{-1} \sum_k e^{ik\Delta} n_{k\sigma} + \text{H.c.} = t^2 N^{-1} \sum_k \cos(k\Delta) n_{k\sigma}. \end{aligned}$$

Determination of the effective exchange between clusters can be done in a way similar to Hubbard's¹⁰ approach to local moment systems. He determined the potential energy for a static configuration of two local neighboring moments as a function of the angle φ these moments form in spin space. The difference in potential energy then is matched against the potential energy of a classical Heisenberg model (with continuous values for φ) with the result $\Delta E(\varphi) = E(\varphi) - E(0) = JS^2 \sin^2 \varphi/2$ (J denotes the Heisenberg coupling constant and S denotes spin). This method is much more justified here than it is in Hubbard's original work: Because we are concerned with clusters we deal with long-wave or low-energy excitations that are slow enough to consider φ a static or fixed parameter and because of the large S of the cluster we can safely assume that the spins behave classically. Once given JS^2 one can determine kT_c because accurate JS^2/kT_c values for the Heisenberg model in the classical limit $S \rightarrow \infty$ are known.¹⁹ What remains is to determine

$$\begin{aligned} E(\varphi) &= \sum_k E_{k\sigma} \\ &= \sum_{k\sigma} \left\{ \frac{1}{2}(\epsilon_{k\sigma} - \mu) - \frac{1}{2}[(\epsilon_{k\sigma} - \mu)^2 + \gamma_{\sigma}^2(\varphi)/\hbar]^{1/2} \right\}. \end{aligned}$$

Since we already know the $\gamma_{\sigma}(\varphi=0)$ we only need to determine $\gamma_{\sigma}(\varphi \neq 0)$ from $\gamma_{\sigma}(\varphi=0)$. Because the physically relevant φ are quite small and the cluster is meant to be large enough to make the boundary or γ terms small, I neglect their influence on the self-consistency equation determining $\gamma_{\sigma}(0)$. (I at first incorporated them only to find out that programs become much more complicated with only small effects as to the results.) Therefore the only change in the γ_{σ} 's is due to the rotation of the orientation of the magnetic moments of neighboring clusters. I assume that the magnetization of the cluster is considered to be the z axis whereas the axis of the

sponds to $\epsilon_{k\sigma}$ for $\epsilon_{k\sigma} < \mu$ and 0 for $\epsilon_{k\sigma} > \mu$ in the limit $\gamma_{\sigma} \rightarrow 0$. The self-consistency equation determining the γ_{σ} 's was derived by assuming that the current somewhere within the cluster should be equal to the corresponding current at the boundary in the homogeneous case:

neighboring cluster shall be rotated around the y axis by an angle φ . Because the γ_{σ} 's represent the influence of the neighboring cluster they are subject to a transformation in spin space. Inserting

$$\bar{c}_{\sigma}^{\pm} = \cos(\varphi/2)c_{\sigma}^{\pm} - \sigma \sin(\varphi/2)c_{-\sigma}^{\pm}$$

into the self-consistency equation and omitting spin-flip terms one has

$$|\gamma_{\sigma}(\varphi)|^2 = \cos^2(\varphi/2)|\gamma_{\sigma}|^2 + \sin^2(\varphi/2)|\gamma_{-\sigma}|^2.$$

The coupling energy $E(\varphi)$ can now be determined; the value fits a $\sin^2 \varphi/2$ curve reasonably well, and so it is possible to determine the parameter JS^2 .

For simplicity I assumed the five d subbands of Fe or the three t_{2g} subbands of Ni to be independent degrees of freedom, each absorbing the thermal energy kT . The subbands (denoted by $\epsilon_{k\sigma}$) were calculated in the tight-binding approximation and fitted to a bandwidth of 3.4 eV (Ni) and 6 eV (Fe) and an exchange splitting of 0.31 eV (Ni) and 1.5 eV (Fe). μ was determined by using occupation numbers $n = 1.8$ (Ni) and 1.4 (Fe) by integration over the tight-binding density of states in Jelitto's²⁰ approximation. Although these assumptions seem to be very simplistic, calculations showed that there is not much change in the results when one arbitrarily alters the band shapes, but that the results are quite sensitive to the occupation number n . This is due to the fact that $\gamma_{\sigma}(0)$ depends essentially on n ($\gamma_{\sigma} = 0$ for $n = 0, 1$ and is large in between). This result is in accord with a recent paper²¹ where it is shown by application of Fulde's local approach to correlation that the magnitude and stability of a local moment in the (hypothetical) paramagnetic phase of transition metals is essentially determined by the band occupation only. Because, as was already said, the calculation of the exchange

forces *within* the cluster establishing the local exchange splitting is not yet ready, the *length* of the cluster cannot be determined and must be treated as a parameter.

The results for kT_c (in electronvolts) are the following:

	Ni	Fe
$h = 3$	0.0481	1.0280
$h = 4$	0.0547	1.7880
$h = 5$	0.1406	3.2128
$h = 6$	0.4130	4.3325

The experimental values are $kT_c = 0.054$ eV (Ni) and $kT_c = 0.090$ eV (Fe). The results show that the ferromagnetic transition in Ni can be understood by the cluster method presented here and by the local band theory which differs only slightly in the prediction of the cluster length for Ni (local band theory, $h = 5$; this work, $h = 4$). For larger cluster dimensions the calculated Curie temperature increases because the cluster is assumed to be rigid whereas actually there are thermal excitations of shorter wavelength. It may also be seen that the Curie temperature of Fe is always too high, indicating that the excitation driving the phase transition may be more localized than can be accounted for in a local band theory. This is in accord with general opinion and can be seen in, e.g., the Rhodes-Wohlfarth plot²² and the fact that Hubbard's¹⁰ recent work which is based on a localized model works much better for Fe than for Ni.

A calculation applying these ideas to the photoemission line shape of Ni, measured with unprecedented resolution by Maetz and Gerhardt,²³ is in progress.

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