Magnetism in transition metals

J. L. Morán-López,* and K. H. Bennemann
Institut für Theoretische Physik, Freie Universität Berlin, 1000 Berlin 33, Germany

M. Avignon
Groupe de Transitions de Phases, Centre National de la Recherche Scientifique, Grenoble, France
(Received 10 October 1980)

By using the Hubbard tight-binding-type Hamiltonian and the cluster Bethe-lattice approximation we calculate for Fe the Curie temperature $T_C = 2250$ K and the temperature dependence of the magnetic moments and the magnetization. Moreover, we show how previous theories for itinerant magnets may be extended to include short-range spin correlations.

I. INTRODUCTION

For many years magnetism in transition metals has been studied intensively. Nevertheless, there remain important problems which have not been solved satisfactorily. The open problems arise from the fact that some of the magnetic properties of transition metals, like the non-half-integral atomic moments, can be accounted for by band theories and other properties, such as the Curie temperature, can be explained only by means of localized models.

Recently, several authors,[1-7] have used an approach to itinerant magnets in which local moments are assumed to exist on each lattice site in both the magnetically ordered and the paramagnetic state. They have shown that the Stoner paramagnetic state underestimates the entropy of the system and therefore overestimates the Curie temperature. The results obtained indicate the significance of short-range spin correlation effects and of quantum effects. For example, Hubbard[5] calculated for Fe a Curie temperature T_C, in a mean-field model. He obtains T_C of the order of 2000 K and a temperature dependence of the magnetization corresponding to spins $s = \infty$. In the following we present a theory which allows us to include spin correlations. This theory is similar to the one described in Ref. 3. The main difference is that this is a finite temperature calculation. We calculate for Fe the Curie temperature and the temperature dependence of the magnetization and of the local magnetic moments.

II. THEORY

We use the Hubbard Hamiltonian in the unrestricted Hartree-Fock (UHF) approximation

$$H = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_{i,\sigma} U \langle n_{i-\sigma} \rangle n_{i\sigma} - \sum_{i} U \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \ , \tag{2.1}$$

where t_{ij} denotes the hopping integral for electronic transitions between lattice sites i and j, σ is the spin index, U is the Coulomb integral and $c_{i\sigma}^{\dagger}$, $c_{i\sigma}$ are the usual creation and annihilation operators for electrons on site i with spin σ. We assumed that the magnetic moments exist on each lattice site and that they point up (+) or down (−) along a specified direction. Then the system of atoms with moments μ_+ and μ_- can be treated like a binary alloy where the lattice sites are occupied either with μ_+ or μ_-.

We denote by $p^{ij}(i,j = +,-)$ the probability of finding two moments μ_i and μ_j as nearest neighbors. Then, the single-site probabilites p^i are given in terms of the p^{ij} by

$$p^i = \sum_j p^{ij} \ . \tag{2.2}$$

Two magnetic order parameters can be defined in terms of the probabilities; a short-range order parameter

$$\xi \equiv 1 - 2(p^{+-} + p^{-+}) \tag{2.3}$$

and a long-range order parameter

$$\eta \equiv p^+ - p^- \ . \tag{2.4}$$

In the complete magnetically ordered state the order parameters take the values $\eta = 1$ and $\xi = 1$ and in the paramagnetic state one finds $\eta = 0$ and $\xi \neq 0$. By using Eqs. (2.3) and (2.4) and the normalization condition, it is possible to write the probabilities p^{ij} and p^i in terms of ξ and η.

The relative average magnitude of the magnetic moment is given by

$$\mu = \frac{\bar{\mu}(T)}{\bar{\mu}(0)} = \frac{p^+ \mu_+ + p^- |\mu_-|}{\bar{\mu}(0)} \ , \tag{2.5}$$

where the magnetic moments μ_+ and μ_- pointing parallel and opposite to the direction of the magneti-

zation are given by

$$\mu_+ = \langle n_\uparrow \rangle^+ - \langle n_\downarrow \rangle^+, \quad \mu_- = \langle n_\uparrow \rangle^- - \langle n_\downarrow \rangle^- \ , \quad (2.6)$$

Here, $\langle n_\sigma \rangle^i$ gives the average number of electrons with spin σ at an atomic site with magnetic moment μ_i. The magnetization is given by

$$M(T) = \frac{p^+ \mu_+(T) + p^- \mu_-(T)}{\mu_+(0)} \ . \quad (2.7)$$

It is worth noticing that the symbols + and − refer to sites with moments up and down, respectively, and ↑ and ↓ refer to the spin of the electrons.

To calculate

$$\langle n_\sigma \rangle^i = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \, \mathrm{Im} G^i_{00,\sigma}(\omega) f(\omega) \ , \quad (2.8)$$

we determine the local Green's function $G^i_{00,\sigma}$ for σ spin electrons at a site with magnetic moment i by

$$(\omega - \epsilon_i^\sigma) G^i_{00,\sigma} = 1 - zt(p^{(i)i} G^i_{10,\sigma} + p^{(i)j} G^j_{10,\sigma}) \quad (2.9)$$

and the $G^i_{10,\sigma}$ are given by

$$\begin{aligned}
(\omega - \epsilon_+^\sigma) G^+_{10,\sigma} &= -tG^+_{00,\sigma} - (z-1)t(p^{(+)+} G^+_{20,\sigma} + p^{(+)-} G^-_{20,\sigma}) \ , \\
(\omega - \epsilon_+^\sigma) G^+_{10,\sigma} &= -tG^-_{00,\sigma} - (z-1)t(p^{(+)+} G^+_{20,\sigma} + p^{(+)-} G^-_{20,\sigma}) \ , \\
(\omega - \epsilon_-^\sigma) G^-_{10,\sigma} &= -tG^+_{00,\sigma} - (z-1)t(p^{(-)+} G^+_{20,\sigma} + p^{(-)-} G^-_{20,\sigma}) \ , \\
(\omega - \epsilon_-^\sigma) G^-_{10,\sigma} &= -tG^-_{00,\sigma} - (z-1)t(p^{(-)+} G^+_{20,\sigma} + p^{(-)-} G^-_{20,\sigma}) \ .
\end{aligned} \quad (2.10)$$

Here z is the coordination number, the Wannier Green's function $G^i_{n0,\sigma}$ refers to lattice sites n and 0 and the probabilities $p^{(i)j}$ are defined by

$$p^{(i)j} \equiv p^{ij}/p^i \ . \quad (2.11)$$

Equations (2.10) can be solved in the Bethe-lattice approximation[8] by defining the four transfer functions for each σ:

$$\gamma^\sigma_{ij} = G^i_{n0,\sigma} / G^j_{(n-1)0,\sigma} \quad (i,j = +,-) \ . \quad (2.12)$$

In the general case ($\xi \neq 0, \eta \neq 0$) the transfer functions γ^σ_{ij} are determined by solving a fourth-order equation. This is not the case for $\xi = 1$, $\eta = 1$ and for $\xi = 0$, $\eta = 0$, where the γ^σ_{ij} are obtained by solving a second- and third-order equation, respectively.

Due to translational invariance[5] it is necessary to have charge neutrality at all atomic sites. This is achieved by modifying the energy levels of the electrons at sites with magnetic moment pointing in the down direction by the amount $\alpha U/2$. Thus, the energy levels of the electrons are given by

$$\epsilon^+_\uparrow = \frac{n - \mu_+}{2} U, \quad \epsilon^+_\downarrow = \frac{n + \mu_+}{2} U$$

and

$$\epsilon^-_\uparrow = \frac{n - \mu_- + \alpha}{2} U, \quad \epsilon^-_\downarrow = \frac{n + \mu_- + \alpha}{2} U \ . \quad (2.13)$$

III. RESULTS

Here, we present results including only long-range order. Thus, we take into account only site probabilites. The parameters used are $\mu_-(T=0) = 2.3$, $U = 0.98$ eV, the bandwidth $W = 4.0$ eV and $n = 7.7$ electrons, which correspond approximately to iron.

In Fig. 1 we present results for the local density of states at sites with magnetic moments μ_+ and μ_- for three different situations, corresponding to $\eta = 1, 0.4$, and 0, respectively. The values for μ_+ and μ_- are obtained in a self-consistent manner, once the values obtained by

$$\mu_+ = \int_{-\infty}^{\epsilon_F} (\rho^+_\uparrow - \rho^+_\downarrow) d\omega \quad (3.1)$$

and

$$\mu_- = \int_{-\infty}^{\epsilon_F} (\rho^-_\uparrow - \rho^-_\downarrow) d\omega$$

and those used in Eqs. (2.13) do not differ. Here,

$$\rho^i_\sigma = -\frac{1}{\pi} \mathrm{Im} G^i_{00,\sigma} \ . \quad (3.2)$$

A similar self-consistent loop is carried out to guarantee charge conservation; i.e.,

$$n = \int_{-\infty}^{\epsilon_F} (p^+ \rho^+_\uparrow + p^+ \rho^+_\downarrow) d\omega = \int_{-\infty}^{\epsilon_F} (p^- \rho^-_\uparrow + p^- \rho^-_\downarrow) d\omega \ . \quad (3.3)$$

In Fig. 2 we show results for μ_+ and μ_- as a function of the long-range order parameter η. We find that $|\mu_-|$ decreases always as a function of η in contrast to the results published by Hasegawa,[4] which violate charge conservation.

In Fig. 3 we present results for the internal energy

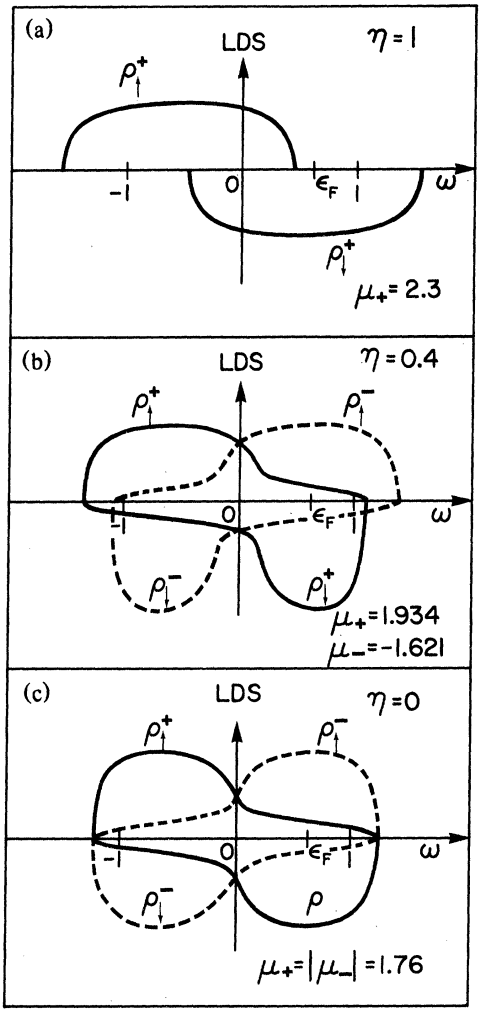

FIG. 1. Results for the electronic density of states ρ_σ^+ and ρ_σ^- for different values of η, μ_+, and μ_-. ϵ_F is the Fermi energy.

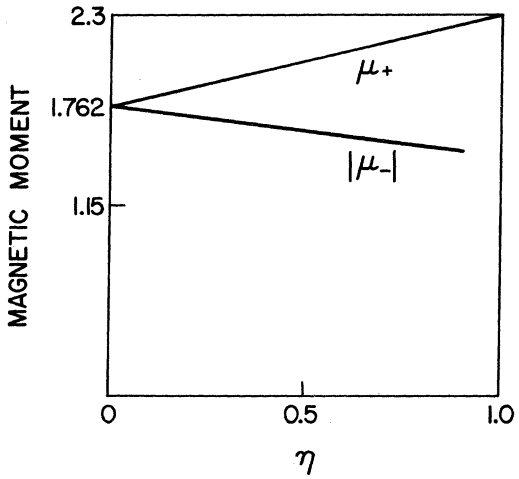

FIG. 2. Results for $\mu_+(\eta)$ and $\mu_-(\eta)$.

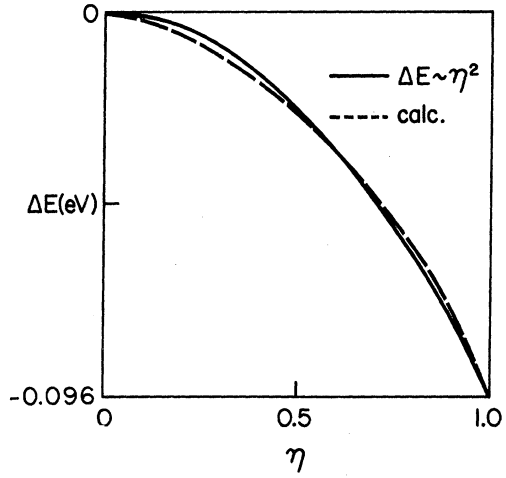

FIG. 3. Results for the internal energy difference $\Delta E(\eta)$.

difference $\Delta E = E(\eta=0) - E(\eta)$. The η dependence is slightly different from the η^2 dependence characteristic of phenomenological theories of order-disorder phenomena.

To find the equilibrium value for the order parameter, we minimize

$$F = \Delta E - TS \ , \tag{3.4}$$

where

$$S = -kN(p^+ \ln p^+ + p^- \ln p^-) \ , \tag{3.5}$$

with respect to η. In Fig. 4 we show the results for the relative average magnetic moment, and for the relative magnetization defined by Eqs. (2.5) and (2.7), respectively. We obtain for the Curie temperature of Fe the result $T_C = 2250$ K.

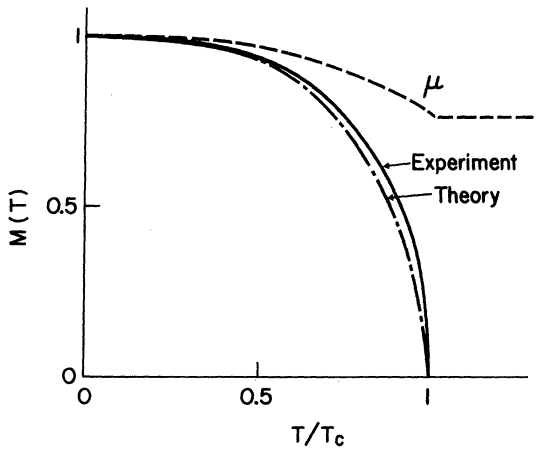

FIG. 4. Results for the temperature dependence of the magnetization $m = M(T)/M(T=0)$ and the average magnetic moment μ.

One expects on general physical grounds that including short-range spin correlations, e.g., $\xi \neq 0$, will decrease T_C towards the experimental value. In phenomenological theories, for example, the Curie temperature calculated in the Bethe approximation is about 10% of the one calculated in a mean-field (Bragg-Williams) theory.[9] Similarly, for $\xi \neq 0$ better agreement with experimental results for $m(T)$ is expected. However, note that our results for $m(T)$ agree much better with experimental results than $m(T)$ calculated by Hubbard.[5] Further improvement of our results is expected from using a more realistic density of states $\rho^{J}_{\sigma}(\omega)$.

ACKNOWLEDGMENT

Helpful discussions with Dr. P. Schlottmann are gratefully acknowledged.

---

*On leave of absence from : Departamento de Física, Centro de Investigacion y de Estudios, Avanzados del IPN, Apdo. Postal 14-740, México 14, D.F., Mexico.

[1]M. Cryot, Phys. Rev. Lett. 25, 871 (1970).
[2]V. Korenman, J. L. Murray, and R. E. Prange, Phys. Rev. B 16, 4032, 4048, 4058 (1977).
[3]S. H. Liu, Phys. Rev. B 17, 3629 (1978).
[4]H. Hasegawa, J. Phys. Soc. Jpn. 46, 1504 (1979).
[5]J. Hubbard, Phys. Rev. B 19, 2626 (1979); 20, 4584 (1979).
[6]L. M. Roth, in *Transition Metals 1977,* edited by M. J. G. Lee, J. M. Perz, and E. Fawcett, IOP Conf. Proc. No. 39 (IOP, Bristol and London, 1978), p. 473.
[7]D. G. Pettifor, J. Magn. Magn. Mater. 15–18, 847 (1980).
[8]R. C. Kittler and L. M. Falicov, Phys. Rev. B 18, 2506 (1978).
[9]C. Domb, Adv. Phys. 9, 149 (1960).