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Variational approach to finite-temperature magnetism

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A theory is presented for magnetism at finite temperatures which includes local electron correlations. It goes beyond the static approximation to the functional-integral method. The theory is based on variational methods. At $T=0$ it reduces to a correlated ground state of the form proposed by Gutzwiller [Phys. Rev. **134**, A293 (1964); **137**, A1726 (1965)]. In the high-temperature limit the static approximation is recovered. A single-site approximation is made in order to make numerical calculations possible. The theory is applied to Fe and Ni. A large reduction of the Curie temperature of Fe is found due to correlations. The amplitude of the local moment is increased by the electron correlations. It hardly changes with temperature in contrast to the results of the static approximation. We also discuss the magnetization-versus-temperature curves, the paramagnetic susceptibility, and the charge fluctuations.

I. INTRODUCTION

A long-standing problem in the theoretical description of magnetism in transition metals and alloys is the incorporation of localized as well as itinerant features of the d electrons. It is well known that the band picture of electrons explains well the noninteger (in units of Bohr magnetons) magnetizations of the ground states,[1] the large cohesive energies,[2] and the large Sommerfeld coefficients γ of the low-temperature specific heat in those systems.[3] On the other hand, for Fe, Co, and Ni the magnetization follows a Brillouin-function form with argument $S=\frac{1}{2}$. The susceptibility is described by a Curie-Weiss law with a Curie constant which is close to the one expected from a Heisenberg Hamiltonian, i.e., a localized model.[4] The specific-heat anomaly in Fe at the Curie temperature T_C is also well explained by a localized description.[5]

One of the difficulties that was encountered previously with the band theory was the much too large values of T_C which were predicted. The key problem was therefore how one could understand, by starting from the microscopic Hamiltonian for the conduction electrons, the large magnetic entropy which is responsible for the finite-temperature effects close to or above T_C. This problem was essentially solved by the application of the functional-integral method.[6–9] This technique was first applied to the Hubbard model by Cyrot.[10] He showed that in both cases, the local moment as well as the band case are contained in a functional-integral formulation, e.g., of the partition function. He also discussed the metal-insulator transition by combining the coherent-potential approximation (CPA) with a saddle-point approximation. This approach was extended by Hubbard[11] and Hasegawa,[12] who avoided the saddle-point approximation by developing a self-consistent single-site theory. In particular, Hasegawa showed[13] how itinerant as well as localized features of the conduction-electron system are generated within a Hubbard model. Their theory has been extensively used and has a wide range of applications. Recent developments of the functional-integral method go beyond the single-site approximation[14,15] and also include the fivefold degeneracy of the d bands[16] and local-environment effects in magnetic alloys.[17,18] Furthermore, Moriya and Takahashi developed a theory of magnetic short-range order by making a suggestive ansatz for the energy functional and its nonlinear dependence on the amplitude of the spin fluctuations.[19] A microscopic theory for that functional within the static approximation was proposed by Moriya and Hasegawa.[20]

All of the above theories which allow for realistic, self-consistent calculations of the different magnetic quantities are based on the static approximation. The latter is basically a high-temperature approximation which has the following shortcomings.

(i) The static approximation does not generally include spin-wave excitations. A recently developed theory by Prange and Korenman[21] describes spin-wave excitations above T_C by going beyond the static approximation and by assuming strong short-range order. The theory, which has been highly stimulating, cannot, however, be considered to properly describe thermodynamical quantities, e.g., the specific heat and the susceptibility of, e.g., Fe.[22–24]

(ii) The static approximation violates a number of thermodynamic relations at $T=0$, such as $(\partial M/\partial T)_{T=0}=0$, $(C_v)_{T=0}=0$, and $(\partial V/\partial T)_{T=0}=0$.[12,25–29] Those relations are not violated when instead of the static approximation a random-phase approximation (RPA) is made. An example is the computational scheme developed by Hertz and Klenin.[30] It can be used to derive the thermodynamic properties of transition metals but it is difficult to calculate, e.g., the dynamical susceptibility with it.

(iii) In the static approximation the free energy reduces at $T=0$ to the Hartree-Fock ground-state energy of the system. This eliminates from consideration the fact that the true ground state of the system also contains electron correlations. Therefore, e.g., the energy difference between a paramagnetic and ferromagnetic ground state is overestimated by the static approximation.

It is the improvement of this last point (iii) that is the main purpose of this paper. Our aim is to generalize the static approximation in such a way that the free energy reduces at $T=0$ to that of the correlated ground state, while for $T\rightarrow\infty$ it goes over into that of the static approximation. Most of the correlations which are contained in available theories of the ground state[31–45] are also present above T_C (or T_N) because the related correlation energies are so large that they are not destroyed by thermal fluctuations. Therefore, one can describe them by assuming that they follow adiabatically the thermodynamic fluctuations. This is done by means of a variational principle and is a central point of the present investigation.

Attempts to describe the changes in the ground state due to correlations go back to Van Vleck[31] and have been studied in more detail by Gutzwiller[32] and Friedel.[35] Over the last few years work has intensified on that problem[36–45] and there is now a physical picture available concerning the size and the character of most of the different ground-state correlations.

In this paper we use the Feynman inequality for the free energy in order to derive variationally an energy functional which goes beyond the static approximation. We consider at present only the simplest case of one orbital per atom and, furthermore, only those correlations which reduce the charge fluctuations at a site (Gutzwiller energy functional). This is certainly a strong simplification. However, a large part of the present investigation does not depend on the specific form of the energy functional which is used. Therefore, we leave for future investigations the use of a functional which corresponds to the local approach[36,38] (LA) and which is not limited by the above restrictions. It was previously used by Oleś and Stollhoff for an estimate of the reduction of the Curie temperature T_C by correlations.[46] They assumed that T_C was proportional to the energy difference between a ferromagnetic and nonmagnetic ground state and calculated the latter within the LA. A similar estimate for the Néel temperature T_N of antiferromagnets was made by Takano and Okiji[47] (for related work see also Oleś[48]). The present theory provides a thermodynamic basis for the computations of T_C and T_N.

This paper is organized as follows. Section II contains a derivation of the energy functional including correlations in the form of a trial function. The variational parameters are determined from Feynman inequalities. In Sec. III expressions are derived from this functional for the energy, entropy, and local moments. The amplitude of the local moment needs particularly careful treatments which are contained in Appendix A. Section IV contains a critical discussion of the validity of the present theory including the limits $T=0$ and $T\rightarrow\infty$. For the purpose of performing numerical calculations a single-site theory is presented in Sec. V. It leads to considerable simplifications because all correlation parameters can then be expressed in terms of the local density of states which is easily calculated within the CPA. The results for the magnetization and susceptibility of Fe and Ni are presented in Sec. VI. A strong reduction in T_C is found due to correlations. The corresponding antiferromagnetic case will be the subject of a separate paper. The enhancement of the amplitude of the local moment due to correlations is pointed out. Finally, Sec. VII contains a summary of our theory as well as a discussion of the effects of orbital degeneracies and possible applications of the theory to other problems.

II. VARIATIONAL APPROACH TO THE ENERGY FUNCTIONAL

We adopt a single-band model Hamiltonian of a form which was first proposed by Gutzwiller[32] and Hubbard,[33]

$$H=\sum_{i,j,\sigma} t_{ij}a_{i\sigma}^{\dagger}a_{j\sigma}+\sum_{i,\sigma}(\varepsilon_i^0-h_i\sigma)n_{i\sigma}+\sum_i U_i n_{i\uparrow}n_{i\downarrow}\ . \tag{2.1}$$

Here t_{ij} is the hopping matrix element between sites i and j. Furthermore, ε_i^0, h_i, and U_i are the atomic energy level, the local magnetic field, and the Coulomb integral at site i, respectively. $a_{i\sigma}^{\dagger}$ ($a_{i\sigma}$) is the creation (annihilation) operator of an electron with spin σ at site i and $n_{i\sigma}=a_{i\sigma}^{\dagger}a_{i\sigma}$ is the occupation-number operator.

The following exact form holds for the free energy F when expressed within the two-field functional-integral scheme:[8,9]

$$e^{-\beta F}=\int\left[\prod_{i=1}^{N}\left[\frac{\beta U_i}{4\pi}\right]^{1/2}d\xi_i\right]e^{-\beta E(\xi,T)}\ . \tag{2.2}$$

The energy functional $E(\xi,T)$ contains the dynamical degrees of freedom of the two fields, i.e.,

$$e^{-\beta E(\xi,T)}=\int\left\{\prod_{i=1}^{N}\left[\left[\frac{\beta U_i}{4\pi}\right]^{1/2}d\zeta_{i0}\prod_{\nu=1}^{\infty}\frac{\beta U_i}{2\pi}d^2\xi_{i\nu}\frac{\beta U_i}{2\pi}d^2\zeta_{i\nu}\right]\right\}\exp\left[-\tfrac{1}{4}\beta\sum_i U_i(\xi_i^2+\zeta_{i0}^2)\right]\mathrm{Tr}(e^{-\beta H^0(\xi,-i\zeta_0)})$$

$$\times\exp\left[\mathrm{Sp}\ln(1-V'\widetilde{G})-2\beta\sum_{i=1}^{N}\sum_{\nu=1}^{\infty}\tfrac{1}{4}U_i(|\xi_{i\nu}|^2+|\zeta_{i\nu}|^2)\right], \tag{2.3}$$

where $\beta=1/k_BT$ and N is the number of sites. $\xi_{i\nu}$ ($\zeta_{i\nu}$) is a fluctuating exchange (charge) field at site i with frequency ν. For brevity we shall set $\xi_i=\xi_{i0}$. The differential $d^2\xi_{i\nu}$ ($d^2\zeta_{i\nu}$) stands for

$$d(\mathrm{Re}\xi_{i\nu})d(\mathrm{Im}\xi_{i\nu})\ [d(\mathrm{Re}\zeta_{i\nu})d(\mathrm{Im}\zeta_{i\nu})]\ .$$

$H^0(\xi,-i\zeta_0)$ is a one-electron Hamiltonian which depends on the static variables $\{\xi_i,-i\zeta_{i0}\}$,

$$H^0(\xi,-i\zeta_0)=\sum_{i,j,\sigma} t_{ij}a^\dagger_{i\sigma}a_{j\sigma} + \sum_{i,\sigma}[\varepsilon_i^0-\mu-\tfrac{1}{2}U_i(i\zeta_{i0}+\xi_i\sigma)] \ . \quad (2.4)$$

The corresponding one-electron Green's function is defined by

$$(\widetilde{G})_{i\nu\sigma,j\nu'\sigma'}=\{[i\omega_\nu-H^0(\xi,-i\zeta_0)]^{-1}\}_{i\sigma,j\sigma}\delta_{\sigma\sigma'}\delta_{\nu\nu'} \ , \quad (2.5)$$

where $\omega_\nu=(2\nu+1)\pi/\beta$. V' is a dynamical scattering potential defined with respect to deviations from the static potential as

$$(V')_{i\nu\sigma,j\nu'\sigma'}=-\tfrac{1}{2}U_i(i\zeta_{i\nu-\nu'}+\xi_{i\nu-\nu'}\sigma) \times(1-\delta_{\nu 0}\delta_{\nu' 0})\delta_{ij}\delta_{\sigma\sigma'} \ . \quad (2.6)$$

The symbol Sp in Eq. (2.3) denotes the trace with respect to frequency and the site and spin indices.

If one neglects the dynamical scattering potential V' the energy functional $E(\xi,\zeta)$ in Eq. (2.2) goes over into that of the static approximation,

$$E_{\text{st}}(\xi,\zeta)=-\beta^{-1}\ln \operatorname{Tr}(e^{-\beta H^0(\xi,\zeta)})-\tfrac{1}{4}\sum_i U_i\{[\zeta_i(\xi)]^2-\xi_i^2\} , \quad (2.7)$$

$$E_{\text{st}}(\xi,\zeta)=-\int d\omega\, f(\omega)N(\omega,\xi)-\tfrac{1}{4}\sum_i U_i\{[\zeta_i(\xi)]^2-\xi_i^2\} , \quad (2.8)$$

$$N(\omega,\xi)\equiv\int^{\omega}d\omega'\rho(\omega',\xi) \ . \quad (2.9)$$

Here $\rho(\omega,\xi)$ is the density of states (DOS) which corresponds to $H^0(\xi,\rho)$. In Eq. (2.8) the local saddle-point approximation for the charge field ζ_i has been adopted. It corresponds to setting $\zeta_i(\xi)=n_i^0(\xi)$, where $n_i^0(\xi)$ is the electron charge at site i which follows from the Hamiltonian $H^0(\xi,\zeta)$. The static approximation within the two-field scheme leads to the correct high-temperature behavior but results in the Hartree-Fock approximation at $T=0$.

Our aim is to include the correlation effects which are also present at $T=0$. This is done by deriving an energy functional $E(\xi,T)$ which goes beyond that of the static approximation. It contains the dynamical degrees of freedom of the fields in an integrated form. For that purpose we introduce a trial energy functional E_t with a corresponding free energy F_t. According to Feynman's inequality it is

$$F\le F_t+\langle E(\xi,T)-E_t(\xi,T)\rangle_t \ , \quad (2.10)$$

where

$$e^{-\beta F_t}\equiv\int\left[\prod_i\left[\frac{\beta U_i}{4\pi}\right]^{1/2}d\xi_i\right]e^{-\beta E_t(\xi,T)} \ , \quad (2.11)$$

$$\langle(\cdots)\rangle_t\equiv\frac{\int\left[\prod_i d\xi_i\right]e^{-\beta E_t}(\cdots)}{\int\left[\prod_i d\xi_i\right]e^{-\beta E_t}} \ . \quad (2.12)$$

According to the physical picture presented in the Introduction we assume that the trial energy functional which goes beyond the static approximation depends on adiabatic parameters $\{\eta_i(\xi,T)\}$

$$E_t=E_t(\xi,\eta(\xi,T),T) \ . \quad (2.13)$$

Minimizing the right-hand side of Eq. (2.10) results in the following conditions:

$$\frac{\partial E_t(\xi,\eta(\xi,T),T)}{\partial\eta_i}=0 \ . \quad (2.14)$$

The appropriate choice of E_t is of crucial importance in the present approach. We shall write for the correlated ground-state wave function $|\psi_0\rangle=Q\,|\phi_0\rangle$, where $|\phi_0\rangle$ is the uncorrelated ground-state wave function and Q is a yet unspecified operator. This form is particularly suitable because it generates $|\psi_0\rangle$ out of a Slater determinant to which the static approximation reduces at $T=0$. We therefore use for E_t an energy functional of the form

$$E_t(\xi,\zeta(\xi,T),\eta(\xi,T),T)=E_{\text{st}}(\xi,\zeta(\xi,T),T)+\langle Q\widetilde{H}Q\rangle_0 \ . \quad (2.15)$$

Here

$$\widetilde{H}=H-\langle H_0\rangle \quad (2.16)$$

and the average $\langle(\cdots)\rangle_0$ is defined through

$$\langle A\rangle_0=\frac{\operatorname{Tr}(e^{-\beta H^0(\xi,\zeta)}A)}{\operatorname{Tr}(e^{-\beta H^0(\xi,\zeta)})} \ . \quad (2.17)$$

As mentioned before, all considerations in this section are general in that they do not require a particular choice for Q. However, when we introduce the single-site approximation and apply the present theory to Fe and Ni we will assume that we have one orbital per site and that Q is of the form

$$Q=\left\langle\prod_i(1-\eta_i O_i)^2\right\rangle_0^{-1/2}\left[\prod_i(1-\eta_i O_i)\right] , \quad (2.18)$$

where

$$O_i=(n_{i\uparrow}-\langle n_{i\uparrow}\rangle_0)(n_{i\downarrow}-\langle n_{i\downarrow}\rangle_0) \ . \quad (2.19)$$

Equation (2.18) corresponds to the Gutzwiller wave function with a slight change in the definition of O_i. Whenever we use the particular form (2.18) for Q in Eq. (2.15) we will refer to E_t as the Gutzwiller type of energy functional and denote it by E_G.

In the following we regard both $\{\zeta_i(\xi,T)\}$ and $\{\eta_i(\xi,T)\}$ as variational parameters. The former builds up the best charge potential and the latter best describes the correlated motion of the electrons in the static exchange fields $\{\xi_i\}$. Equation (2.14) is then supplemented by a second equation so that

$$\frac{\partial}{\partial\eta_i(\xi)}\langle Q\widetilde{H}Q\rangle_0=0 \ , \quad (2.20)$$

$$\frac{\partial}{\partial\zeta_i(\xi)}(E_{\text{st}}+\langle Q\widetilde{H}Q\rangle_0)=0 \ . \quad (2.21)$$

The corresponding free energy is approximated by

$$F_t=-\beta^{-1}\ln\int\left[\prod_i\left[\frac{\beta U_i}{4\pi}\right]^{1/2}d\xi_i\right]e^{-\beta E_t(\xi)}\ . \tag{2.22}$$

At $T=0$ this expression reduces to

$$F_t=E_t(\xi^*,\zeta(\xi^*),\eta(\xi^*))\ , \tag{2.23}$$

where the $\{\xi_i^*\}$ are determined from

$$\frac{\partial}{\partial\xi_i}(E_{\mathrm{st}}+\langle Q\tilde{H}Q\rangle_0)=0. \tag{2.24}$$

III. ENERGY, ENTROPY, AND LOCAL MOMENTS

In this section we derive expressions for the entropy, energy, local charges, and local moments within the variational approach outlined above. An important point is that all expressions are general in the sense that they do not depend on the special form of Q and the operator set $\{O_i\}$. Only the variational properties of Eqs. (2.20) and (2.21) are used in the following derivations.

The entropy is calculated from $-\partial F_t/\partial T$:

$$S=\beta^2\left\langle\frac{\partial E_t}{\partial\beta}\right\rangle+\beta\langle E_t\rangle+\ln\int\left[\prod_i\left[\frac{\beta U_i}{4\pi}\right]^{1/2}d\xi_i\right]e^{-\beta E_t}-\tfrac{1}{2}N\ , \tag{3.1}$$

where the average $\langle(\cdots)\rangle$ is defined by Eq. (2.12). The temperature dependence of E_t via $\zeta_i(\xi,T)$ and $\eta_i(\xi,T)$ can be neglected when the derivative $\partial E_t/\partial\beta$ $(=\partial E_{\mathrm{st}}/\partial\beta+\partial\langle Q\tilde{H}Q\rangle_0/\partial\beta)$ is computed because of the variational conditions. After some manipulations we obtain the final expression

$$S=-\int d\omega\langle\rho(\omega,\xi)\rangle\{[1-f(\omega)]\ln[1-f(\omega)]+f(\omega)\ln f(\omega)\}+\ln\int\left[\prod_i\left[\frac{\beta U_i}{4\pi}\right]^{1/2}d\xi_i\right]e^{-\beta(E_t-\langle E_t\rangle)}-\tfrac{1}{2}N+\beta^2\left\langle\frac{\partial}{\partial\beta}\langle Q\tilde{H}Q\rangle_0\right\rangle\ . \tag{3.2}$$

The first term is the well-known entropy of a one-electron system with a temperature-dependent DOS. The second term is the renormalized magnetic entropy. The third term is a consequence of the chosen prefactor $(\beta U_i/4\pi)^{1/2}$. The last term describes an additional entropy which is due to the dependence of $\langle Q\tilde{H}Q\rangle_0$ on T.

The energy is obtained from Eqs. (3.1) and (2.22). One finds

$$\begin{aligned}\langle H-\mu N\rangle=&\int d\omega f(\omega)\omega\langle\rho(\omega,\xi)\rangle\\&-\tfrac{1}{4}\sum_i U_i\{\langle[\zeta_i(\xi)]^2\rangle-\langle\xi_i^2\rangle+2/\beta U_i\}\\&+\left\langle\left[\langle Q\tilde{H}Q\rangle_0+\beta\frac{\partial}{\partial\beta}\langle Q\tilde{H}Q\rangle_0\right]\right\rangle\ .\end{aligned} \tag{3.3}$$

Here we have used the expression (2.8). The first and second terms denote the energy within the static approximation with a renormalization due to correlations taken into account in the thermal averages. The last term represents the explicit correlation correction.

The local charge $\langle n_i\rangle$ is obtained from

$$\langle n_i\rangle=\frac{\partial}{\partial\varepsilon_i^0}F_t=\left\langle\frac{\partial}{\partial\varepsilon_i^0}(E_{\mathrm{st}}+\langle Q\tilde{H}Q\rangle_0)\right\rangle\ . \tag{3.4}$$

Because of Eqs. (2.20) and (2.21) there are no contributions from $\partial\zeta_j(\xi)/\partial\varepsilon_i^0$ and $\partial\eta_j(\xi)/\partial\varepsilon_i^0$. Furthermore,

$$\frac{\partial}{\partial\varepsilon_i^0}E_{\mathrm{st}}=\frac{\partial}{\partial\varepsilon_i^0}\left[E_{\mathrm{st}}+\tfrac{1}{4}\sum_i U_i\{[\zeta_i(\xi)]^2-\xi_i^2\}\right]\ . \tag{3.5}$$

On the right-hand side ε_i^0 appears only in the combination

$$\varepsilon_i^0-\mu+\tfrac{1}{2}U_i[\zeta_i(\xi)-\xi_i\sigma]-h_i\sigma\ .$$

Therefore, the derivative $\partial/\partial\varepsilon_i^0$ can be replaced by $(2/U_i)\partial/\partial\zeta_i$. Then we obtain

$$\frac{\partial}{\partial\varepsilon_i^0}E_{\mathrm{st}}=\frac{2}{U_i}\frac{\partial}{\partial\zeta_i}E_{\mathrm{st}}+\zeta_i(\xi)\ . \tag{3.6}$$

In the same way,

$$\frac{\partial}{\partial\varepsilon_i^0}\langle QHQ\rangle_0=\left\langle Q\frac{\partial\tilde{H}}{\partial\varepsilon_i^0}Q\right\rangle_0+\frac{2}{U_i}\frac{\partial}{\partial\zeta_i}\langle Q\tilde{H}Q\rangle_0\ , \tag{3.7}$$

where

$$\frac{\partial\tilde{H}}{\partial\varepsilon_i^0}\equiv\frac{\partial H}{\partial\varepsilon_i^0}-\left\langle\frac{\partial H}{\partial\varepsilon_i^0}\right\rangle_0=n_i-\langle n_i\rangle_0\equiv\tilde{n}_i\ . \tag{3.8}$$

From Eqs. (3.4), (3.6), and (3.7) one obtains the expression

$$\langle n_i\rangle=\langle\zeta_i(\xi)\rangle+\langle\langle Q\tilde{n}_iQ\rangle_0\rangle\ . \tag{3.9}$$

Here again use has been made of Eq. (2.21).

Similar considerations lead to the following expression for the local moment:

$$\begin{aligned}\langle m_i\rangle=&-\frac{\partial}{\partial h_i}F_t=\langle\xi_i\rangle+\langle\langle Q\tilde{m}_iQ\rangle_0\rangle\\&-\frac{2}{U_i}\left\langle\frac{\partial}{\partial\xi_i}(E_{\mathrm{st}}+\langle Q\tilde{H}Q\rangle_0)\right\rangle\ ,\end{aligned} \tag{3.10}$$

where $\tilde{m}_i\equiv m_i-\langle m_i\rangle_0$. The last term vanishes after integrating by parts. Therefore,

$$\langle m_i\rangle=\langle\xi_i\rangle+\langle\langle Q\tilde{m}_iQ\rangle_0\rangle\ . \tag{3.11}$$

The thermal averages of the square of the local charge and the local moment are obtained by using the relations

$$\left.\begin{matrix}\langle n_i^2\rangle \\ \langle m_i^2\rangle\end{matrix}\right\}=\langle n_i\rangle \pm 2\langle n_{i\uparrow}n_{i\downarrow}\rangle \ , \tag{3.12}$$

$$\langle n_{i\uparrow}n_{i\downarrow}\rangle=\frac{\partial}{\partial U_i}F_t \ . \tag{3.13}$$

The last equation is rewritten as

$$\begin{aligned}\langle n_{i\uparrow}n_{i\downarrow}\rangle=&-\frac{1}{2\beta U_i}+\tfrac{1}{4}(\langle[\zeta_i(\xi)]^2\rangle-\langle\xi_i^2\rangle)\\&+\langle\langle Q\delta(n_{i\uparrow}n_{i\downarrow})Q\rangle_0\rangle\\&+\left\langle\left[\frac{\zeta_i}{U_i}\frac{\partial}{\partial\zeta_i}+\frac{\xi_i}{U_i}\frac{\partial}{\partial\xi_i}\right]E_t\right\rangle ,\end{aligned} \tag{3.14}$$

where

$$\delta(n_{i\uparrow}n_{i\downarrow})\equiv n_{i\uparrow}n_{i\downarrow}-\langle n_{i\uparrow}n_{i\downarrow}\rangle_0 \ .$$

The derivative $\partial E_t/\partial\zeta_i$ vanishes due to Eq. (2.21) and $\langle\xi_i\partial E_t/\partial\xi_i\rangle=-T$ after integrating by parts. Thus,

$$\begin{aligned}\langle n_{i\uparrow}n_{i\downarrow}\rangle=&\frac{1}{4}\left[\langle[\zeta_i(\xi)]^2\rangle-\langle\xi^2\rangle+\frac{2}{\beta U_i}\right]\\&+\langle\langle Q\delta(n_{i\uparrow}n_{i\downarrow})Q\rangle_0\rangle \ .\end{aligned} \tag{3.15}$$

We obtain then the following final expressions for $\langle n_i^2\rangle$ and $\langle m_i^2\rangle$:

$$\begin{aligned}\left.\begin{matrix}\langle n_i^2\rangle \\ \langle m_i^2\rangle\end{matrix}\right\}=&\langle\zeta_i(\xi)\rangle\pm\frac{1}{2}\left[\langle[\zeta_i(\xi)]^2\rangle-\langle\xi_i^2\rangle+\frac{2}{\beta U_i}\right]\\&+\left\langle\left\langle Q\times\begin{Bmatrix}\delta(n_i^2)\\ \delta(m_i^2)\end{Bmatrix}\times Q\right\rangle_0\right\rangle ,\end{aligned} \tag{3.16}$$

where $\delta(n_i^2)\equiv n_i^2-\langle n_i^2\rangle_0$ and $\delta(m_i^2)\equiv m_i^2-\langle m_i^2\rangle_0$. There is a second way of deriving expressions for $\langle n_i^2\rangle$ and $\langle m_i^2\rangle$. One can introduce Coulomb as well as exchange parameters into the interaction term of Eq. (2.1), i.e., by writing

$$\sum_i(U_in_i^2-J_im_i^2)/4 \ ,$$

and regarding F_t as a function of $\{U_i\}$ and $\{J_i\}$. Then the relations hold:

$$\left.\begin{matrix}\langle n_i^2\rangle \\ \langle m_i^2\rangle\end{matrix}\right\}=4\times\begin{Bmatrix}\dfrac{\partial}{\partial U_i}\\ -\dfrac{\partial}{\partial J_i}\end{Bmatrix}\times F_t(U,J) \ . \tag{3.17}$$

If we were to use the true free energy F instead of the approximate one, F_t, both methods for determining $\langle n_i^2\rangle,\langle m_i^2\rangle$, i.e., through Eqs. (3.12) or (3.17), would yield the same results. This is not the case, however, when F_t is used. Later we shall use the expressions (3.16) because they produce better results (for a detailed discussion of the reasons consult Appendix A). Note that Eq. (3.17) leads to the well-known formula for the amplitude of the local moment (LM) within the static approximation

$$\langle m_i^2\rangle=\langle\xi_i^2\rangle-\frac{2}{\beta J_i} \ . \tag{3.18}$$

IV. RANGE OF VALIDITY OF THE THEORY

We wish to discuss the range of validity of the variational theory formulated above by imposing the following two restrictions.

(a) We approximate the $\zeta_i(\xi)$ by those of the static approximation, i.e.,

$$\zeta_i(\xi)\approx n_i^0(\xi)=\int d\omega f(\omega)\rho_i(\omega,\xi) \ , \tag{4.1}$$

where $\rho_i(\omega,\xi)$ is the local DOS belonging to H^0 [see Eq. (2.4)].

(b) The Fermi distribution function in the trial functional $\langle QHQ\rangle_0$ is replaced by a step function.

These conditions facilitate the proofs of the following statements.

(1) The free energy F_t is lower than $F_{\rm st}$, the free energy in the static approximation

$$F_t\le F_{\rm st}+\langle\langle Q\tilde{H}Q\rangle_0\rangle_{\rm st}\le F_{\rm st} \ , \tag{4.2}$$

where $\langle(\cdots)\rangle_{\rm st}$ implies an average (2.12) with E_t replaced by $E_{\rm st}(\xi)$. The first inequality is just the Feynman inequality for F_t with the trial functional $E_{\rm st}(\xi)$. The second inequality is due to the fact that the correlation energy $\langle QHQ\rangle_0$ is negative for any $\{\xi_i\}$.

(2) At $T=0$, F_t gives an upper bound of the exact value E_0. It is instructive to compare it also with the energy $\langle H\rangle_t$, which is obtained when the expectation value of H is exactly calculated with respect to the original Gutzwiller wave function $|\psi_t\rangle=Q|\phi_{\rm HF}\rangle$. Here, $|\phi_{\rm HF}\rangle$ is the Hartree-Fock ground-state wave function. The following inequalities hold at $T=0$:

$$\begin{aligned}E_0\le\langle H\rangle_t(\xi_t,\eta_t(\xi_t))&\le E_t(\xi^*,\eta^*(\xi^*))\\&\le\langle H\rangle_t(\xi_{\rm HF},\eta_t(\xi_{\rm HF})) \ .\end{aligned} \tag{4.3}$$

Here, ξ_t is the exchange field in $|\phi_{\rm HF}\rangle$ which minimizes $\langle H\rangle_t$ and $\xi_{\rm HF}$ is the one which minimizes the Hartree-Fock energy. The first inequality follows from the variational character of $|\psi_t\rangle$. The second and third inequalities result immediately from the relation between $\langle H\rangle_t$ and E_t [see Eqs. (2.15) and (2.80)]

$$\begin{aligned}\langle H\rangle_t=&E_t(\xi,\eta(\xi))-\tfrac{1}{4}\sum_i U_i[\xi_i-m_i^0(\xi)]^2\\&\le E_t(\xi,\eta(\xi)) \ .\end{aligned} \tag{4.4}$$

Here, m_i^0 is the local magnetization which follows from H^0. When ξ_t equals 0 or $\xi_{\rm HF}$ then $\langle H\rangle_t=E_t$. In order to evaluate $\langle H\rangle_t$ one must assume a specific form for the operator Q and must know how to evaluate $\langle Q\tilde{H}Q\rangle$. (See

Refs. 36 and 38.)

(3) In the high-temperature limit the free energy F_t agrees with the one of the static approximation as it should,

$$F_t \rightarrow F_{\mathrm{st}} \quad \text{as } T \rightarrow \infty \ . \tag{4.5}$$

This is seen as follows. Let us consider the case of a half-filled band and rewrite the free energy as

$$e^{-\beta F_t} = e^{-\beta F_{\mathrm{st}}} \int \left[\prod_i d\xi_i \right] p(\xi) e^{-\beta \langle Q\tilde{H}Q \rangle_0} \ . \tag{4.6}$$

Here,

$$p(\xi) = \exp[-\beta E_{\mathrm{st}}(\xi)] \Big/ \int \left[\prod_i d\xi_i \right] \exp[-\beta E_{\mathrm{st}}(\xi)]$$

is the probability functional of the static approximation. It broadens and flattens as the temperature increases. Therefore, at high temperatures the thermal average puts the largest weight on correlation corrections $\langle Q\tilde{H}Q \rangle_0$ with large values $|\xi_i|$. But in the presence of large exchange splittings the probability for double occupancy of a site is very small because one of the atomic spin states is pushed above the Fermi level. In that case there are no electron correlations on a site. This means that $\langle Q\tilde{H}Q \rangle_0 \approx 0$ for large values of $\{\xi_i\}$. Therefore, Eq. (4.6) leads to the result (4.5). For this argument the condition (b) is essential since the Fermi distribution function due to the independent-particle excitations in $\langle QHQ \rangle_0$ would introduce a finite probability for double occupancy of a site even at high temperatures.

(4) The theory given reduces to the correct atomic limit at $T=0$ and $T=\infty$, except for an underestimation of the energy by $U/8$ at $T=\infty$, which is due to the saddle-point approximation for the charge field. This is easily demonstrated with the help of the single-site approximation which we refer to the next section.

V. SINGLE-SITE APPROXIMATION

The next step consists of simplifying the theory so that actual calculations become possible. This is achieved by making a single-site approximation (SSA).

The SSA within the static approximation is well established.[11,12] An effective medium $\{\mathscr{L}_{i\sigma}^{-1}\}$, which describes spatially averaged one-electron states, is inserted into the diagonal part of the Hamiltonian (2.4). The energy functional $E_{\mathrm{st}}(\xi)$ is expanded with respect to the deviations (scattering potentials) from the effective medium $\{\mathscr{L}_{i\sigma}^{-1}(\omega)\}$. To zeroth order one uses the effective medium only. The first-order correction terms consist of the energy functionals of "impurities" embedded in the effective medium. All higher-order terms are neglected in the SSA. It is

$$E_{\mathrm{st}}(\xi) = \int d\omega f(\omega) \frac{1}{\pi} \operatorname{Im} \operatorname{Tr}[\ln(\mathscr{L}^{-1} - t) + \ln F] + \sum_i E_i^{(s)}(\xi_i) \ , \tag{5.1}$$

$$E_i^{(s)}(\xi_i) = \int d\omega f(\omega) \frac{1}{\pi} \operatorname{Im} \sum_\sigma \ln(L_{i\sigma}^{-1} - \mathscr{L}_{i\sigma}^{-1} + F_{i\sigma}^{-1}) - \tfrac{1}{4} U_i \{[\zeta_i(\xi)]^2 - \xi_i^2\} \ , \tag{5.2}$$

where

$$(F)_{i\sigma j\sigma'} = F_{i\sigma} \delta_{ij} \delta_{\sigma\sigma'} \ , \tag{5.3}$$

$$F_{i\sigma} = [(\mathscr{L}^{-1} - t)^{-1}]_{i\sigma i\sigma} \ , \tag{5.4}$$

$$L_{i\sigma}^{-1} = \omega - [\varepsilon_i^0 - \mu + \tfrac{1}{2} U_i \zeta_i(\xi) - \tfrac{1}{2} U_i \xi_i \sigma] \ . \tag{5.5}$$

In the following we will assume for Q the special form given by Eq. (2.18). In order to distinguish the following special form with the previous general considerations we shall replace in the following the index t (trial) in the energy functional and the other quantities by the index G (Gutzwiller functional). After Q has been specified a serious difficulty consists in calculating expressions such as $\langle QHQ \rangle_0$. By making use of Wick's theorem all correlation corrections presented in the previous sections can be written as sums of products of different contractions. The following expressions are obtained when all correlations between operators on different sites are neglected:[32,49,50]

$$\langle Q\tilde{H}Q \rangle_0 = \sum_i E_i^{(c)}(\xi_i) \ , \tag{5.6}$$

$$E_i^{(c)}(\xi_i) = \frac{-2\eta_i \langle O_i\tilde{H} \rangle_0 + \eta_i^2 \langle O_i\tilde{H}O_i \rangle_0}{1 + \eta_i^2 \langle O_i^2 \rangle_0} \ . \tag{5.7}$$

When there is translational invariance this is equivalent to the so-called $\mathbf{R}=0$ approximation introduced by Friedel and co-workers.[45] Explicit expressions for $\langle O_i\tilde{H} \rangle_0$ and $\langle O_i\tilde{H}O_i \rangle_0$ are given in Appendix B. It should be noted that for any configuration of the exchange fields $\{\xi_i\}$ all quantities on the right-hand side of Eqs. (5.6) and (5.7) can be expressed by the local density of states $\rho_{i\sigma}(\omega\xi)$. The latter is approximated by the CPA-DOS,

$$\rho_{i\sigma}(\omega,\xi) = -\frac{1}{\pi} \operatorname{Im}[L_{i\sigma}^{-1} - \mathscr{L}_{i\sigma}^{-1} + F_{i\sigma}^{-1}]^{-1} \ . \tag{5.8}$$

Note that the above-mentioned fact also allows for applying the present type of approach to alloys.

From Eqs. (5.1) and (5.6) we obtain the free energy in the SSA

$$F_G = \int d\omega f(\omega) \frac{1}{\pi} \operatorname{Im} \operatorname{Tr}[\ln(\mathscr{L}^{-1} - t) + \ln F] - T \sum_i \ln \int \left[\frac{\beta U_i}{4\pi} \right]^{1/2} d\xi_i e^{-\beta E_i(\xi_i)} \ , \tag{5.9}$$

$$E_i(\xi_i) = E_i^{(s)}(\xi_i) + E_i^{(c)}(\xi_i) \ . \tag{5.10}$$

The correlation parameter η_i is obtained analytically from $\partial E_i^{(c)}/\partial \eta_i = 0$, i.e.,

$$\eta_i(\xi_i) = \frac{-\langle O_i\tilde{H}O_i \rangle_0 + (\langle O_i\tilde{H}O_i \rangle_0^2 + 4\langle O_i\tilde{H} \rangle_0^2 \langle O_i^2 \rangle_0)^{1/2}}{2\langle O_i\tilde{H} \rangle_0 \langle O_i^2 \rangle_0} \ . \tag{5.11}$$

The correlation-correction terms in Eqs. (3.9), (3.11), and

(3.16) are similarly obtained in the SSA. One finds

$$\langle n_i \rangle = \langle n_i^0(\xi) \rangle + \left\langle \frac{2\eta_i^2 \langle O_i^2 \rangle_0 [1-n_i^0(\xi)]}{1+\eta_i^2 \langle O_i^2 \rangle_0} \right\rangle , \tag{5.12}$$

$$\langle m_i \rangle = \langle \xi_i \rangle - \left\langle \frac{2\eta_i^2 \langle O_i^2 \rangle_0 m_i^0(\xi)}{1+\eta_i^2 \langle O_i^2 \rangle_0} \right\rangle , \tag{5.13}$$

$$\langle n_i^2 \rangle = \langle n_i^0(\xi) \rangle + \frac{1}{2} \left[\langle [n_i^0(\xi)]^2 \rangle - \langle \xi_i^2 \rangle + \frac{2}{\beta U_i} \right] + \left\langle \frac{4\langle O_i^2 \rangle_0 \{ -\eta_i + \eta_i^2 [1-n_i^0(\xi)] \}}{1+\eta_i^2 \langle O_i^2 \rangle_0} \right\rangle , \tag{5.14}$$

$$\langle m_i^2 \rangle = \langle n_i^0(\xi) \rangle - \frac{1}{2} \left[\langle [n_i^0(\xi)]^2 \rangle - \langle \xi_i^2 \rangle + \frac{2}{\beta U_i} \right] + \left\langle \frac{4\eta_i \langle O_i^2 \rangle_0}{1+\eta_i^2 \langle O_i^2 \rangle_0} \right\rangle . \tag{5.15}$$

Here, the average $\langle (\cdots) \rangle$ is with respect to $E_i(\xi_i)$. The approximation $\zeta_i(\xi) \approx n_i^0(\xi)$ has been adopted.

The coherent potentials $\{ \mathscr{L}_{i\sigma}^{-1} \}$ in Eqs. (5.1) to (5.15) are determined in such a way that the t matrix caused by the scattering potentials $\{ L_{i\sigma}^{-1}(\xi) - \mathscr{L}_{i\sigma}^{-1} \}$ vanishes when the thermal average is taken,[51,52]

$$\left\langle \frac{1}{L_{i\sigma}^{-1}(\xi) - \mathscr{L}_{i\sigma}^{-1} + F_{i\sigma}^{-1}} \right\rangle = F_{i\sigma} . \tag{5.16}$$

The approximation

$$\langle \xi_i^{2n+k} \rangle \approx \langle \xi^2 \rangle^n \langle \xi \rangle^k \quad (k=0,1)$$

simplifies considerably the numerical calculation.[12,15] It leads to

$$\sum_{\nu=\pm} q_{i\nu} \{ [L_{i\sigma}(\nu x_i)]^{-1} - \mathscr{L}_{i\sigma}^{-1} + F_{i\sigma}^{-1} \}^{-1} = F_{i\sigma} , \tag{5.17}$$

$$q_{i\nu} = \frac{1}{2} \left[1 + \nu \frac{\langle \xi_i \rangle}{x_i} \right] , \tag{5.18}$$

where

$$\left. \begin{matrix} \langle \xi_i \rangle \\ x_i^2 \end{matrix} \right\} \equiv \int d\xi \times \left\{ \begin{matrix} \xi \\ \xi^2 \end{matrix} \right\} \times e^{-\beta E_i(\xi)} \Big/ \int d\xi \, e^{-\beta E_i(\xi)} . \tag{5.19}$$

In the following we consider two simple cases, a ferromagnetic state and an antiferromagnetic state. In a ferromagnetic system all sites are equivalent. Therefore, the coherent potential $\mathscr{L}_{i\sigma}^{-1}$ does not depend on the particular site, and the site index can be dropped in Eqs. (5.1) to (5.19). The coherent Green function F_σ is calculated from

$$F_\sigma(\mathscr{L}_\sigma^{-1}) = \int \frac{\rho_0(\varepsilon) d\varepsilon}{\mathscr{L}_\sigma^{-1} - \varepsilon} , \tag{5.20}$$

where $\rho_0(\varepsilon)$ is the DOS corresponding to the transfer matrix t_{ij}.

In the antiferromagnetic state with the sublattices (+) and ($-$), two kinds of coherent potentials $\mathscr{L}_\sigma^{(+)-1}$ and $\mathscr{L}_\sigma^{(-)-1}$ must be introduced. However, because of symmetry relations such as $\mathscr{L}_\sigma^{(-)} = \mathscr{L}_{-\sigma}^{(+)}$ all quantities and self-consistent equations can be described by the coherent potentials of the (+) site only. The coherent Green function $F_\sigma^{(+)}$ is obtained from

$$F_\sigma^{(+)} = \left[\frac{\mathscr{L}_{-\sigma}^{(+)-1}}{\mathscr{L}_\sigma^{(+)-1}} \right]^{1/2} \int \frac{\rho_0(\varepsilon) d\varepsilon}{(\mathscr{L}_+^{(+)-1} \mathscr{L}_-^{(+)-1})^{1/2} - \varepsilon} , \tag{5.21}$$

when $\epsilon_{\mathbf{k}} = -\epsilon_{\mathbf{k}+\mathbf{Q}}$ is assumed for the dispersion following from $\{ t_{ij} \}$ (cubic symmetry).[53-55] Here $\mathbf{Q} = 2\pi(1,0,0)/a$, with a being the lattice parameter of the unit cell.

Equation (5.12) determines the chemical potential. Equations (4.1) and (5.11) determine $\zeta(\xi)$ and $\eta(\xi)$. $\langle \xi \rangle$, x, and $\mathscr{L}_\sigma^{-1}$ are obtained self-consistently from Eqs. (5.17) and (5.19) for given electron number n, Coulomb interaction U, d-band width W and model DOS $\rho_0(\varepsilon)$.

VI. APPLICATIONS: Fe AND Ni

We present in this section the results of numerical calculations for ferromagnetic Fe and Ni within the single-site approximation. The Fermi distribution function is replaced by a step function everywhere since this leads only to minor changes. We begin with Fe. The d-electron number and the d-band width are taken as $n=1.44$ $(=7.2/5)$ and $W=0.45$ Ry.[56,57] The model density of states for the bcc structure is shown in the inset of Fig. 4.

Figure 1 shows the ground-state magnetization as a function of U. It is seen that correlations reduce it (spin fluctuations). With the present choice of parameters a first-order phase transition takes place at $2U/W=1.75$. The experimentally observed magnetization $\langle m \rangle = 0.443$ $(=2.216/5)\mu_B$ is obtained for $U=0.52$ Ry and we shall use this value for U in the following. In order to obtain the same $\langle m \rangle$ in the HF approximation a $U_{\text{eff}}=0.357$ Ry $(\cong 0.7U)$ is required. The last relation is consistent with previous findings of Oleś and Stollhoff.[46,49]

The correlation energy functional $E_c(\xi)$ [see Eq. (5.7)] and related quantities are shown in Fig. 2 for the ferromagnetic and paramagnetic states. $E_c(\xi)$ has a minimum near $\xi=0$ since the external field ξ reduces the

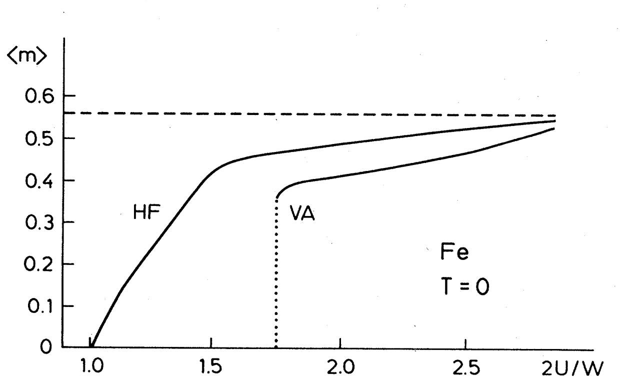

FIG. 1. Ground-state magnetizations as a function of the Coulomb interaction U (in units of half the bandwidth) for Fe. VA refers to the present variational approach while HF refers to the Hartree-Fock approximation. The dashed line shows the asymptotic value while the dotted line indicates the first-order transition.

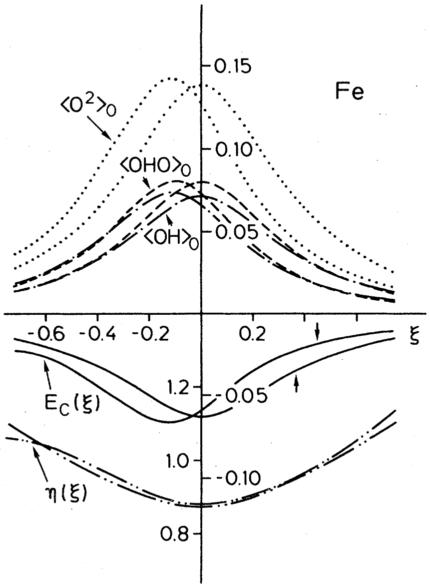

FIG. 2. Various correlation parameters and the correlation energy functional for Fe in the ferromagnetic state ($T/T_C=0.45$) and in the paramagnetic state ($T/T_C=1.34$). The left-hand scale refers to $\eta(\xi)$. The arrows indicate the value of E_c at $(\langle\xi^2\rangle)^{1/2}$. The curves which are symmetric around $\xi=0$ refer to the paramagnetic state.

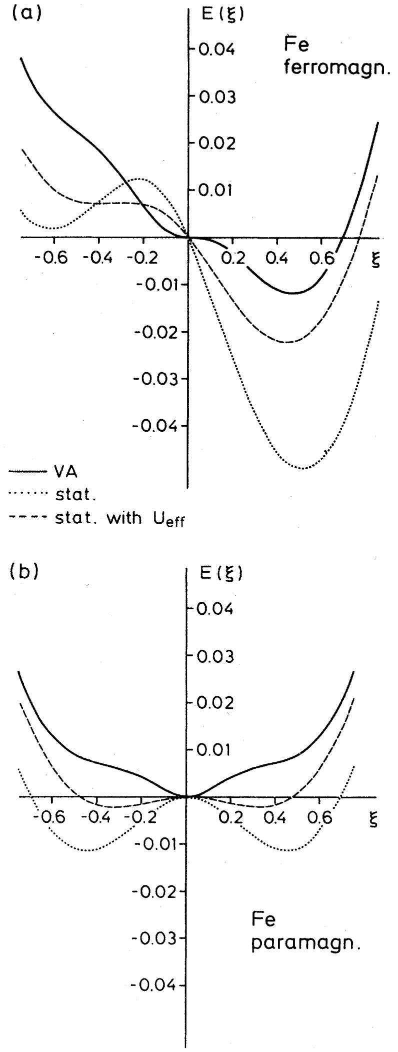

FIG. 3. $E(\xi)$ for Fe in the (a) ferromagnetic state ($2T/W=0.0042$) and (b) paramagnetic state ($2T/W=0.0127$). VA refers to the present approach, while stat. and stat. with U_{eff} refer to the static approximation with the same U as in VA and $U_{\text{eff}}=0.69U$, respectively. The results for U_{eff} are for $2T/W=0.0267$.

probability of double occupancies of sites. The variational parameters $\eta(\xi)$ are appreciably large. Despite this the renormalization factor is $\eta^2\langle O_i^2\rangle$ is smaller than 0.03 [see Eq. (5.7)].

The functional $E_G(\xi)$ differs considerably from $E_{\text{st}}(\xi)$ because of the strong ξ dependence of $E_c(\xi)$. This is shown in Fig. 3. Even in the paramagnetic state, $E_G(\xi)$ has only one minimum in contrast to the results of the static approximation.

The magnetization-versus-temperature curve is shown in Fig. 4. Correlations reduce the Curie temperature by a factor of 3. However, the effects of correlations can be simulated by making the static approximation, but using an effective U_{eff} which is smaller than the true value of U. In the past U_{eff} has been chosen to be consistent either with (i) the observed ground-state magnetization,[11,12,16,58] (ii) the value calculated from a local spin-density functional theory at $T=0$,[16,58] or (iii) the exchange splitting observed in the angular-resolved photoemission experiments.[59] The results of the static approximation with U_{eff} chosen according to (i) is also shown in Fig. 4. When correlations are included the reduced magnetization curve is close to a Brillouin-function form. Near T_C it is larger than a Brillouin-function form with argument $S=\frac{1}{2}$, which is in agreement with experiments.

The susceptibility is calculated by applying an infinitesimal external field. It follows a Curie-Weiss law. The effective magneton number m_{eff} divided by the ground-state magnetization is about 1.75 and close to that of the static approximation. The experimental value is 1.44 (Ref. 4).

Local electron correlations also enhance the amplitude of the local moment by several percent as compared with that within the static approximation. The value 0.73 at $T=0$ is close to the atomic value 0.75. The electron correlations also reduce the T dependence of the amplitude. It is found that

$$(\langle m^2\rangle)^{1/2}(T_C)/(\langle m^2\rangle)^{1/2}(T=0)=0.99$$

as compared with 0.96 in the static approximation. The reductions of the charge fluctuations $\langle(\delta n)^2\rangle$ can be also read from Fig. 4.

Next we consider Ni. The model DOS is shown in the inset of Fig. 8. The parameters chosen are $n=1.8$ ($=9.0/5$) and $W=0.35$ Ry.[60] The ground-state magnetization is shown in Fig. 5. There is a second-order transition with increasing values of U. In the following we

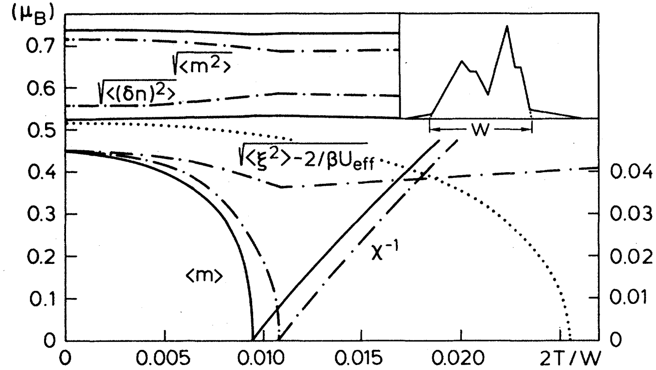

FIG. 4. Magnetization $\langle m\rangle$, inverse susceptibility χ^{-1}, amplitude of local moment $(\langle m^2\rangle)^{1/2}$, and charge fluctuation $(\langle(\delta n)^2\rangle)^{1/2}$ for Fe as a function of temperature. ——: the different quantities within the variational approach. · · · ·: $\langle m\rangle$ in the static approximation. —·—·—·: the different quantities in the static approximation but with $U_{\rm eff}=0.694U$. Also shown is $(\langle\xi^2\rangle-2/\beta U_{\rm eff})^{1/2}$. The scale on the right-hand side refers to χ^{-1}. The model DOS is shown in the inset together with the definition of d-band width W.

choose $U=0.60$ Ry, which gives rise to $\langle m\rangle=0.123$ $(=0.615/5)\mu_B$. A value $U_{\rm eff}=0.49$ Ry must be chosen in order to reproduce the observed zero-temperature magnetization within the HF approximation.

Since the number of holes is small in Ni, the correlation energy contribution is smaller than in the case of Fe. The curves $E_c(\xi)$ are flatter as shown in Fig. 6. The energy functionals in various approximations are presented in Fig. 7. The present result is similar to that of the static approximation with $U_{\rm eff}$.

The temperature dependences of the magnetization, paramagnetic susceptibility, the amplitude of local moment, and the charge fluctuations are shown in Fig. 8. The reduction of T_C is about 20% as compared with the static approximation. The magnetization curve and the susceptibility are well described by the static approximation with $U_{\rm eff}$. This is understandable because the field dependence of $E_c(\xi)$ is very small and therefore $E_c(\xi)$ does not change the shape of the total-energy functional. The susceptibility follows a Curie-Weiss law and $m_{\rm eff}/\langle m\rangle(T=0)\cong 3.5$. This should be compared with the experimental value 2.68.[61] Values between 2.4 and ~ 3.0 have been reported in previous calculations based on the two-field method.[12,15]

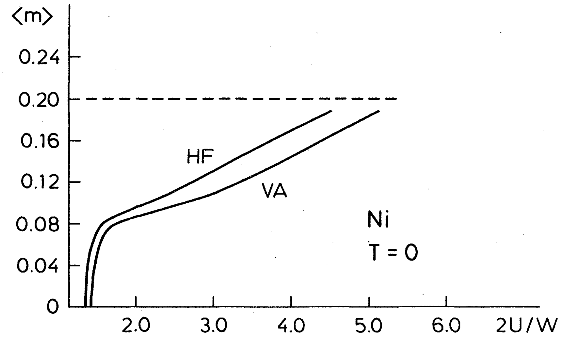

FIG. 5. Magnetization curve for the ground state of Ni as a function of $2U/W$. The notation is the same as in Fig. 1.

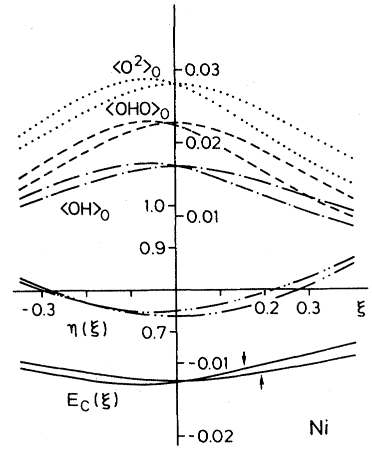

FIG. 6. Various correlation parameters and the correlation energy functional for Ni in the ferromagnetic state $(T/T_C=0.35)$ and the paramagnetic state $(T/T_C=1.16)$.

The amplitude calculated from Eq. (3.16) is more than 3.5 times larger than that obtained from Eq. (3.18). The inclusion of the correlations enhances the amplitude $\langle m^2\rangle$ by a few percent. It is close to the atomic value 0.449. There is no anomaly in $\langle m^2\rangle$ and $\langle(\delta n)^2\rangle$ at T_C. The amplitude is almost temperature independent, $(\langle m^2\rangle)^{1/2}(T_C)/(\langle m^2\rangle)^{1/2}(T=0)=1.01$. This is consistent with the theoretical analysis of the thermal-expansion coefficient of Ni.[62,63]

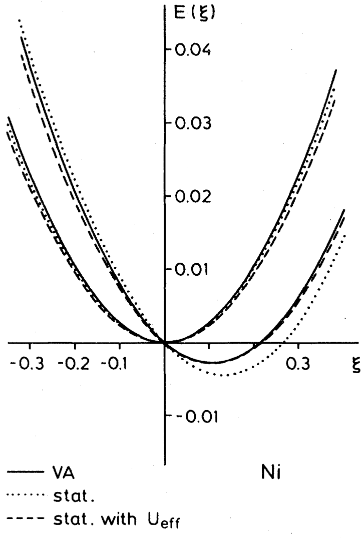

FIG. 7. The energy functional for Ni in the ferromagnetic state $(2T/W=0.0054)$ and the paramagnetic state $(2T/W=0.0181)$. The curve of the static approximation in the paramagnetic state is drawn at $2T/W=0.0217$.

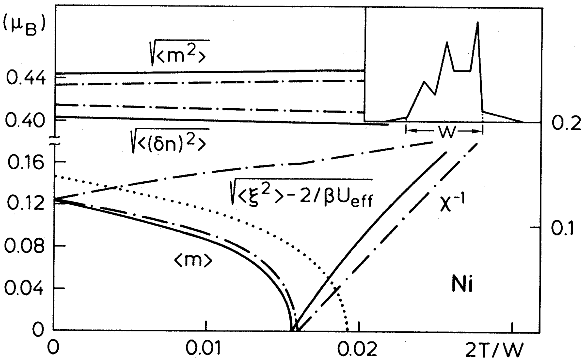

FIG. 8. Magnetization, inverse susceptibility, amplitude of local moment, and charge fluctuation for Ni as a function of temperature. The notation is the same as in Fig. 4.

VII. DISCUSSION AND SUMMARY

We have developed a variational theory for finite temperatures which goes beyond the static approximation. At $T=0$ the theory reduces to the Gutzwiller ground state. Therefore, it cures the main discrepancies between the previously employed static approximation and the zero-temperature many-body theories. In the high-temperature limit the present approach goes over into the static approximation. To enable us to perform numerical calculations a single-site approximation was made. Calculations were done for Fe and Ni within the single-band model. The Curie constant was found to be the same as in the static approximation. The double minimum structure of the energy functional for Fe disappears when local electron correlations are taken into account. The reductions in T_C due to correlations are 65% for Fe and 20% for Ni. Once we adopt the static approximation with U_{eff} chosen in such a way that it fits the observed $T=0$ magnetization, the reduction in T_C is 10% for Fe and negligible in Ni. We expect that these conclusions hold also in a model in which the fivefold degeneracy of the d orbitals is taken into account.

For an understanding of the experimentally observed Curie temperature of $T_C=1044$ K (Ref. 64) for Fe we present the following rough estimate. We start out from a recent extension to the case of degenerate orbitals which Hasegawa gave in his theory.[16] With a U_{eff} chosen to fit the observed magnetization for Fe $2.2\mu_B$ he obtained a Curie temperature of 3000 K. Local correlations reduce T_C by 10% (see Fig. 4). A further reduction by 25% is obtained when instead of a step function the Fermi distribution function is used.[65] Magnetic short-range order results in a further reduction by 35%, when it is due to the nearest-neighbor spin correlation as in a Heisenberg model.[66] We use this estimate here because the amplitudes of the local moments which we obtain in the present model are close to the atomic ones. All these effects then lower T_C to 1300 K. Furthermore, Hasegawa's theory does not account for the transverse quantum degrees of freedom of the atomic spin. Actually the entropy is always ln2 in the atomic limit of his theory instead of ln3 for Fe with $S=1$.[67] Therefore, a further decrease of T_C on the order of 10% is expected, bringing it down to approximately 1200 K.

In Ni there is no reduction of T_C as compared with the static approximation using U_{eff} (see Fig. 8). Also the entropy is not underestimated as in Fe. After inclusion of the Fermi functions Hasegawa[59] obtained $T_C=700$ K. Reducing this value by 30% due to short-range spin correlations of the Heisenberg type[66] results in $T_C\cong 500$ K. This agrees reasonably well with the experimental value of 630 K.[64]

It is desirable to further test the present theory by using for the operator Q more general forms than given by Eq. (2.19). A form which corresponds to the LA would include the fivefold degeneracy of the d orbitals and correlations between them. Such an extension would also include the Hund's rule correlations at low temperatures and their gradual decrease as T increases sufficiently. On the other hand, the suppression of charge fluctuations due to local correlations changes little with temperature because of the large correlation energy gain.

Local correlations also modify strongly the cohesive properties as compared with the static approximation and relative stabilities of different structural phases of Fe.[35,68] A more detailed analysis of the thermodynamics and the cohesive properties based on the present theory and extensions of it will be discussed in a separate paper. Localization due to electron correlations is also responsible for the $3s$ inner-core spectra of $3d$ transition metals showing atomic splittings, in spite of the fact that the d-band width is comparable to the coupling constant between d and core electrons.[69–72]

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APPENDIX A: SUITABLE EXPRESSION FOR $\langle m^2\rangle$

We wish to explain here the reason why, within the present approach, Eq. (3.12) gives better results than Eq. (3.17). Let us consider the amplitude of the local moment in the static approximation and in particular the case $T=0$, where the approximation worsens. Equation (3.12) is reduced to

$$\langle m_i^2\rangle=n_i^0(\xi^*)-\tfrac{1}{2}[n_i^0(\xi^*)^2-m_i^0(\xi^*)^2]\ , \tag{A1}$$

and Eq. (3.17) to

$$\langle m_i^2\rangle=m_i^0(\xi^*)^2\ , \tag{A2}$$

where $\xi_i^*=m_i^0(\xi^*)$. Both (A1) and (A2) describe the correct atomic limit for the half-filled band. However, Eq. (A2) gives the wrong result, $\langle m_i^2\rangle=0$, in the delocalized limit, while Eq. (A1) calculated from Eq. (3.12) gives the exact result, $\langle m_i^2\rangle=\frac{1}{2}$. The failure of (A2) originates from the fact that at $T=0$, $F_{\mathrm{st}}(U,J)$, which is used in Eq. (3.17), reduces to the Hartree-Fock energy $\langle H\rangle_{\mathrm{HF}}(U,J)$ only when $U=J$,

$$F_{\mathrm{st}}(U,J)=\langle H\rangle_{\mathrm{HF}}(U,J)-\tfrac{1}{4}\sum_{i}(U_i-J_i)\sum_{\sigma}n_{i\sigma}^{0}(1-n_{i\sigma}^{0})\ . \tag{A3}$$

Thus,

$$\frac{\partial}{\partial U_i}F_{\mathrm{st}}(U,U)=\frac{\partial}{\partial U_i}\langle H\rangle_{\mathrm{HF}}(U,U)\ , \tag{A4}$$

$$\frac{\partial}{\partial J_i}F_{\mathrm{st}}(U,J)\neq\frac{\partial}{\partial J_i}\langle H\rangle_{\mathrm{HF}}(U,J)\ . \tag{A5}$$

The Hartree-Fock approximation is correct up to first order in U and J. Therefore, the right-hand side of Eqs. (A4) and (A5) result in the correct value in the delocalized limit. Equation (A5) implies that $\langle m_i^2\rangle$ as obtained from Eq. (3.17) does not lead to the correct result in the delocalized limit. The same also holds true when the correlation energy $\langle QHQ\rangle_0$ is taken into account because it is of higher order with respect to U and J.

APPENDIX B: EVALUATION OF VARIOUS LOCAL EXPECTATION VALUES

The expectation values $\langle Q\widetilde{H}Q\rangle_0$, $\langle Q\widetilde{n}_iQ\rangle_0$, $\langle Q\widetilde{m}_iQ\rangle_0$, $\langle Q\delta(n_i^2)Q\rangle_0$, and $\langle Q\delta(m_i^2)Q\rangle_0$ can be evaluated within the single-site approximation without any assumptions about the crystal structure

$$\begin{aligned}\langle O_i\widetilde{H}O_i\rangle_0=\langle O_i\widetilde{H}^{0}(\xi)O_i\rangle_0&\\+\langle O_i\widetilde{H}\rangle_0\{&-[\zeta_i(\xi)-n_i^0(\xi)][1-n_i^0(\xi)]\\&-[\xi_i-m_i^0(\xi)]m_i^0(\xi)\\&+[1-2n_{i\uparrow}^0(\xi)][1-2n_{i\downarrow}^0(\xi)]\}\ ,\end{aligned} \tag{B1}$$

$$\begin{aligned}\langle O_i\widetilde{H}^{0}(\xi)O_i\rangle_0=\sum_{\sigma}n_{i-\sigma}^{0}(\xi)[1-n_{i-\sigma}^{0}(\xi)]&\\\times\bigg[n_{i\sigma}^{0}(\xi)\int d\omega[1-f(\omega)]^2\omega\rho_{i\sigma}(\omega,\xi)&\\-[1-n_{i\sigma}^{0}(\xi)]&\\\times\int d\omega\,[f(\omega)]^2\omega\rho_{i\sigma}(\omega,\xi)\bigg]&\ ,\end{aligned} \tag{B2}$$

$$\langle O_i\widetilde{H}\rangle_0=U_i\langle O_i^2\rangle_0\ , \tag{B3}$$

$$\langle O_i^2\rangle_0=n_{i\uparrow}^0(\xi)[1-n_{i\uparrow}^0(\xi)]n_{i\downarrow}^0(\xi)[1-n_{i\downarrow}^0(\xi)]\ , \tag{B4}$$

$$\langle O_i\widetilde{n}_iO_i\rangle_0=2\langle O_i^2\rangle_0[1-n_i^0(\xi)]\ , \tag{B5}$$

$$\langle O_i\widetilde{m}_iO_i\rangle_0=-2\langle O_i^2\rangle_0m_i^0(\xi)\ , \tag{B6}$$

$$\langle O_i\widetilde{n}_i\rangle_0=\langle O_i\widetilde{m}_i\rangle_0=0\ , \tag{B7}$$

$$\langle O_i\delta(n_i^2)O_i\rangle_0=4\langle O_i^2\rangle_0[1-n_i^0(\xi)]\ , \tag{B8}$$

$$\langle O_i\delta(m_i^2)O_i\rangle_0=0\ , \tag{B9}$$

$$\langle O_i\delta(n_i^2)\rangle_0=-\langle O_i\delta(m_i^2)\rangle_0=2\langle O_i^2\rangle_0\ . \tag{B10}$$

Here, $\rho_{i\sigma}(\omega\xi)$ is the local DOS for the one-electron Hamiltonian $H^0(\xi,\zeta)$ as defined by Eq. (2.4). Equations (B5) to (B10) have been used in the derivation of Eqs. (5.12) to (5.14).

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[1] R. M. Bozorth, *Ferromagnetism* (Van Nostrand, Princeton, 1968).

[2] K. A. Gschneidner, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16.

[3] M. Dixon, F. E. Hoare, T. M. Holden, and D. E. Moody, Proc. R. Soc. London, Ser. A **285**, 561 (1965).

[4] W. Sucksmith and R. R. Pearce, Proc. R. Soc. London, Ser. A **167**, 189 (1938).

[5] G. Inden, Physica **103B**, 82 (1981).

[6] R. L. Stratonovich, Dokl. Akad. Nauk SSSR **115**, 1097 (1958) [Sov. Phys.—Dokl. **2**, 416 (1958)].

[7] J. Hubbard, Phys. Rev. Lett. **3**, 77 (1959).

[8] W. E. Evanson, J. R. Schrieffer, and S. Q. Wang, J. Appl. Phys. **41**, 1199 (1970).

[9] J. R. Schrieffer, W. E. Evanson, and S. Q. Wang, J. Phys. (Paris) Colloq **32**, C1-1 (1971).

[10] M. Cyrot, Phys. Rev. Lett. **25**, 871 (1970); J. Phys. (Paris) **33**, 125 (1972).

[11] J. Hubbard, Phys. Rev. B **19**, 2626 (1979); **20**, 4584 (1979); **23**, 5974 (1981).

[12] H. Hasegawa, J. Phys. Soc. Jpn. **46**, 1504 (1979); **49**, 178 (1980).

[13] H. Hasegawa, Solid State Commun. **31**, 597 (1979).

[14] H. Hasegawa, Solid State Commun. **38**, 401 (1981).

[15] Y. Kakehashi, J. Phys. Soc. Jpn. **50**, 1505 (1981); **50**, 3620 (1981).

[16] H. Hasegawa, J. Phys. F **13**, 1915 (1983).

[17] Y. Kakehashi, J. Phys. Soc. Jpn. **51**, 94 (1982).

[18] Y. Kakehashi, J. Magn. Magn. Mater. **37**, 189 (1983).

[19] T. Moriya and Y. Takahashi, J. Phys. Soc. Jpn. **45**, 397 (1978).

[20] T. Moriya and H. Hasegawa, J. Phys. Soc. Jpn. **48**, 1490 (1980).

[21] R. E. Prange and V. Korenman, Phys. Rev. B **19**, 4691 (1979); **19**, 4698 (1979).

[22] B. S. Shastry, D. M. Edwards, and A. P. Young, J. Phys. C **14**, 1665 (1981).

[23] T. Moriya, J. Phys. Soc. Jpn. **51**, 420 (1982).

[24] T. Oguchi, K. Terakura, and N. Hamada, J. Phys. F **13**, 145 (1983).

[25] J. C. Kimball and J. R. Schrieffer, in International Conference on Magnetism and Magnetic Materials, Chicago, 1971 (unpublished).

[26] K. K. Murata and S. Doniach, Phys. Rev. Lett. **29**, 285 (1972).

[27] K. K. Murata, Phys. Rev. B **12**, 282 (1975).

[28] Y. Kakehashi, J. Phys. Soc. Jpn. **50**, 2236 (1981).

[29] J. H. Samson, J. Phys. (Paris) **45**, 1675 (1984).

[30] J. A. Hertz and M. A. Klenin, Phys. Rev. B **10**, 1084 (1974).

[31] J. H. Van Vleck, Rev. Mod. Phys. **25**, 220 (1953).

[32] M. C. Gutzwiller, Phys. Rev. **134**, A293 (1964); **137**, A1726

(1965).

[33]J. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963); **277**, 237 (1964); **281**, 401 (1964).

[34]J. Kanamori, Prog. Theor. Phys. **30**, 275 (1963).

[35]J. Friedel, in *The Physics of Metals. 1. Electrons,* edited by J. M. Ziman (Cambridge University Press, Cambridge, England, 1969), Chap. 8; J. Friedel and C. M. Sayers, J. Phys. (Paris) **38**, 697 (1977).

[36]G. Stollhoff and P. Fulde, Z. Phys. B **29**, 231 (1978); J. Chem. Phys. **73**, 4548 (1980).

[37]T. Ogawa and K. Kanda, Z. Phys. B **30**, 355 (1978).

[38]T. Kaplan, P. Horsch, and P. Fulde, Phys. Rev. Lett. **49**, 889 (1982).

[39]L. Hedin and B. L. Lundqvist, J. Phys. C **4**, 2064 (1971).

[40]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[41]O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[42]L. M. Roth, Phys. Rev. **186**, 426 (1969).

[43]J. A. Hertz and D. M. Edwards, J. Phys. F **3**, 2174 (1973); **3**, 2191 (1973).

[44]A. Liebsch, Phys. Rev. Lett. **43**, 1431 (1980); Phys. Rev. B **23**, 5203 (1981).

[45]G. Treglia, F. Ducastelle, and D. Spanjaard, Phys. Rev. B **21**, 3729 (1980); F. Kajzar and J. Friedel, J. Phys. (Paris) **39**, 397 (1978).

[46]A. M. Oleś and G. Stollhoff, Phys. Rev. B **29**, 314 (1984).

[47]H. Takano and A. Okiji, J. Phys. Soc. Jpn. **50**, 2891 (1981).

[48]A. M. Oleś, Phys. Rev. B **28**, 327 (1983).

[49]A. M. Oleś, Phys. Rev. B **23**, 271 (1981).

[50]G. Stollhoff and P. Thalmeier, Z. Phys. B **43**, 13 (1981).

[51]B. Velický, S. Kirkpatrick, and H. Ehrenreich, Phys. Rev. **175**, 747 (1968).

[52]H. Shiba, Prog. Theor. Phys. **46**, 77 (1971).

[53]E.-Ni Foo and H. Amar, Phys. Rev. Lett. **25**, 1748 (1970).

[54]M. Plischke and D. Mattis, Phys. Rev. B **7**, 2430 (1973).

[55]A. K. Gupta, D. M. Edwards, and A. C. Hewson, J. Phys. C **8**, 3207 (1975).

[56]J. F. Janak and A. R. Williams, Phys. Rev. B **14**, 4199 (1976).

[57]O. Gunnarsson, Physica **91B**, 329 (1977).

[58]Y. Kakehashi, J. Phys. Soc. Jpn. **50**, 2251 (1981).

[59]H. Hasegawa, J. Phys. F **14**, 1235 (1984).

[60]D. G. Pettifor, Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) **1**, 305 (1977).

[61]S. Arajs and R. V. Colvin, J. Phys. Chem. Solids **24**, 1233 (1963).

[62]Y. Kakehashi, J. Phys. Soc. Jpn. **50**, 2236 (1981); **51**, 3183 (1982).

[63]A. J. Holden, V. Heine, and J. H. Samson, J. Phys. F **14**, 1005 (1984).

[64]J. Crangle and G. M. Goodman, Proc. R. Soc. London, Ser. A **321**, 477 (1971).

[65]Y. Kakehashi, J. Phys. Soc. Jpn. **50**, 1925 (1981).

[66]C. Domb and M. F. Sykes, Proc. R. Soc. London, Ser. A **240**, 214 (1957).

[67]Y. Kakehashi, Phys. Rev. B **31**, 3104 (1985).

[68]G. Stollhoff, in *Proceedings of a Workshop on 3d Metallic Magnetism* (Institut Max von Laue—Paul Langevin, Grenoble, 1983).

[69]C. S. Fadley and D. A. Shirley, Phys. Rev. A **2**, 1109 (1970).

[70]S. Hüfner and G. K. Wertheim, Phys. Rev. B **7**, 2333 (1973); Phys. Lett. **51**, 299 (1975).

[71]F. R. McFeely, S. P. Kowalczyk, L. Ley, and D. A. Shirley, Solid State Commun. **15**, 1051 (1974).

[72]D. C. Kemeney and N. J. Shevchik, Solid State Commun. **17**, 255 (1975).