Range of validity of the simple alloy model for magnetism in transition metals

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The range of validity of the simple alloy model for magnetism in transition metals is studied. By assuming that the local magnetic moments point up or down along a given direction, we analyzed the stability of configurations with various degrees of magnetic order, i.e., from the perfect ferromagnet to the paramagnetic disordered moment state. The electronic structure is solved within the coherent-potential approximation and for two different model density of states. In particular, results are presented for the behavior of the magnetic moments, the magnetic phase diagram, and the Curie temperature. The shortcomings of the alloy model are discussed by comparison with Hubbard's recent theory of magnetism. It is shown how to extend the simple-alloy-model theory to include the important magnetic moment fluctuations taken into account by Hubbard.

I. INTRODUCTION

The magnetic properties of transition metals have been a puzzling subject for a long time. The problem arises from the fact that these metals present properties that can be understood on the basis of two completely different theories, i.e., the band and the localized models. Recently, this problem has been partially solved by models in which local moments formed by itinerant electrons in a Hubbard Hamiltonian are assumed to exist.[1-6] The simplest model of those is comprised of the assumption that the local moments point up or down along a given direction. At zero temperature all the moments point in the up direction, and as the temperature is raised some of the moments flip to the opposite direction. Then, the Curie temperature T_C is reached when the number of magnetic moments pointing up and down is the same. This is the main difference with the Stoner model, in which T_C is obtained only when the magnitude of the magnetic moments vanishes.

In this model,[5] the magnitude of the magnetic moments depends on the degree of magnetic order and it must be evaluated self-consistently. Then, in this simple picture, there are two contributions to the change in magnetization as the temperature increases; the first one arises from the fact that the number of magnetic moments pointing in both directions is changing, and the second from the fact that the magnitude of the moments itself is also changing.

This model includes only two kinds of magnetic moments. Consequently, the thermodynamics of the magnetic transition can be treated as in binary-alloy theory. The simplest approximation is to consider only site probabilities. If p_i $(i=+,-)$ denotes the probability of finding an atom with magnetic moment pointing in the ith direction, then a long-range-order parameter can be defined by

$$\eta = p_+ - p_- \ . \tag{1.1}$$

The completely ferromagnetic state corresponds to $\eta=1$ and the moment-disordered paramagnetic state to $\eta=0$. Partially ordered configurations correspond to $0<\eta<1$.

This model has been applied successfully to a system with parameters corresponding to iron.[5] The question we address in this work is as follows: Do self-consistent solutions exist for the whole range of η and for the whole phase diagram?

Since regarding the ensemble of local magnetic moments as a fictitious alloy is very useful for the physical interpretation of magnetism in transition metals, it is of interest to understand the limitations of such an alloy model. These limitations are investigated below.

Heine *et al.*[6] studied the conditions necessary for the existence of a disordered local moment (DLM) phase, which in our model would correspond to $\eta=0$. By comparing this condition to the Stoner criterion, they showed that there are regions where only the DLM or the ferromagnetic configuration is possible.

Here, we study the stability of partially ordered ferromagnetic configurations. The electronic structure is solved by means of the coherent-potential approximation (CPA) and for two-model density of states. We also show how the energy difference between the completely ordered $(\eta=1)$ and the disordered $(\eta=0)$ states, which can be related to the Curie temperature, depends on the local density of states and on the Hamiltonian's parameters.

In Sec. II we present the model and the calculation. The results are shown and discussed in Sec. III. In the Appendix we derive a formal expression determining the limit of applicability of the simple alloy model.

II. MODEL AND CALCULATION

We consider the Hubbard Hamiltonian in the unrestricted Hartree-Fock 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, $c_{i\sigma}^{\dagger}, c_{i\sigma}$ are the creation and annihilation operators for electrons on site i with spin σ, and $\langle n_{i\sigma}\rangle$ is the average number of electrons with spin σ at an atomic site i. In order to compare these results with those obtained with similar theories,[1-4] we do not take into account intra-atomic exchange interaction, and we scale the occupation numbers and the Coulomb integral by a factor of 5 and $\frac{1}{5}$, respectively, to represent the effects of a fivefold degenerate band. Some possible effects due to e_g and t_{2g} subbands are discussed later also.

For a system with n_i electrons per site

$$n_i=\langle n_{i\uparrow}\rangle+\langle n_{i\downarrow}\rangle \ , \tag{2.2}$$

and defining the magnetic moment at that site i by

$$\mu_i=\langle n_{i\uparrow}\rangle-\langle n_{i\downarrow}\rangle \ , \tag{2.3}$$

we can rewrite the Hamiltonian in the form

$$H=\sum_{i,j,\sigma} t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+\sum_{i}\tfrac{1}{2}U(n_i+\mu_i)n_{i\downarrow} +\sum_{i}\tfrac{1}{2}U(n_i-\mu_i)n_{i\uparrow}-\sum_{i}\tfrac{1}{4}U(n_i^2-\mu_i^2) \ . \tag{2.4}$$

Note that Eq. (2.4), and consequently Eq. (2.1), implies the assumption that a local moment exists at a site for a time long compared to the electron hopping time. In the other limit, one should proceed differently[7] to determine μ.

Now, if we allow that the magnetic moments μ_i point only in two directions, μ_i equal to μ^+ and μ^- respectively, we can solve the electronic structure in a similar way to the binary-alloy problem. In this case, there is only diagonal disorder and the energy levels for electrons with spin up and down are given by

$$\epsilon_{\uparrow}^{i}=\tfrac{1}{2}U(n_i-\mu_i)$$

and (2.5)

$$\epsilon_{\downarrow}^{i}=\tfrac{1}{2}U(n_i+\mu_i) \ ,$$

respectively. The probability of finding an atom with atomic level ϵ_{σ}^{i} is p_i. We have then the case of a binary alloy with concentration $p_+(p_-=1-p_+)$, whose electronic structure can be solved within the translational-symmetry-preserving CPA,[8,9] for example. This approximation permits the determination of the local moments without breaking the translational symmetry of the system.

In order to see how the results depend on the shape of the local density of states, we studied two cases that can be solved analytically. We take the well-known elliptic density of states

$$\rho_1^0(\omega)=\frac{2}{\pi}(1-\omega^2)^{1/2} \ , \tag{2.6}$$

which is similar to the density of states obtained in the Bethe lattice method[10] and

$$\rho_2^0(\omega)=\frac{1}{\pi}\left[\frac{\omega+\frac{3}{2}}{\frac{1}{2}-\omega}\right]^{1/2} \ , \quad -\tfrac{3}{2}\le\omega\le+\tfrac{1}{2} \ . \tag{2.7}$$

This model density of states is asymmetric and has some similarity to the face-centered-cubic lattice type of band.[11,12] In Fig. 1 we show these model density of states.

The CPA equations for the elliptic density of states are discussed in detail in Velický *et al.*[9] Here we give only the equation for $\rho_2^0(\omega)$. The Hilbert transform of ρ_2^0 is given by

$$F_2^0(z)=\int_{-\infty}^{+\infty} d\omega(z-\omega)^{-1}\rho_2^0(\omega) =-1+\left[\frac{z+\frac{3}{2}}{z-\frac{1}{2}}\right]^{1/2} \ . \tag{2.8}$$

This function corresponds to the pure-metal case. The function for the alloy F_2 can be expressed in terms of F_2^0 by

$$F_2(z)=F_2^0(z-\Sigma) \ , \tag{2.9}$$

where Σ is the self-energy containing the information about the scattering corrections to the effective alloy Hamiltonian. Using Eq. (2.9) and the self-consistency equation[8]

$$\Sigma_{\sigma}(z)=\epsilon_{\sigma}-[\epsilon_{\sigma}^{+}-\Sigma_{\sigma}(z)]F_{2,\sigma}(z)[\epsilon_{\sigma}^{-}-\Sigma_{\sigma}(z)] \ , \tag{2.10}$$

one obtains the third-order equation

$$A_0F_{2,\sigma}^3+A_1F_{2,\sigma}^2+A_2F_{2,\sigma}+A_3=0 \ , \tag{2.11}$$

where

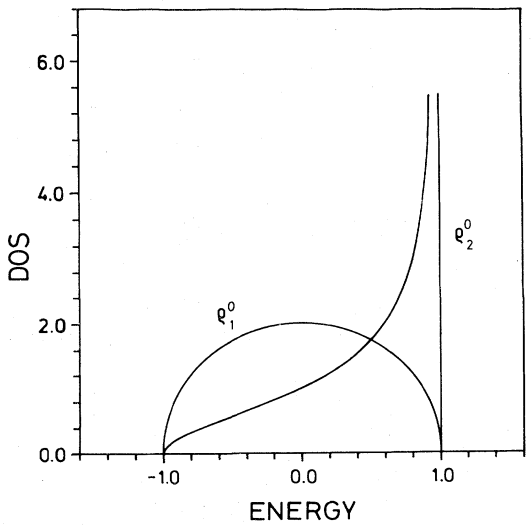

FIG. 1. Two input local density of states given by Eqs. (2.6) and (2.7).

$$A_0=(z-\tfrac{1}{2}-\epsilon_\sigma^+)(z-\tfrac{1}{2}-\epsilon_\sigma^-)\ ,$$
$$A_1=4A_0+z-\tfrac{1}{2}-\epsilon_\sigma\ ,$$
$$A_2=4A_0+2(\epsilon_\sigma^+ +\epsilon_\sigma^-)-4\epsilon_\sigma\ ,$$
$$A_3=-4(z+\epsilon_\sigma-\epsilon_\sigma^+-\epsilon_\sigma^-)\ , \tag{2.12}$$

and

$$\epsilon_\sigma=p_+\epsilon_\sigma^+ +p_-\epsilon_\sigma^-\ .$$

Equation (2.11) is solved for real z, yielding either three real roots or one real root and two complex roots. In the latter case, the one in the lower-half complex plane is the physical one. The local Green's function can then be obtained from

$$G_\sigma^i(z)=F_{2,\sigma}(z)\{1-[\epsilon_\sigma^i-\Sigma_\sigma(z)]F_{2,\sigma}(z)\}^{-1}\ , \tag{2.13}$$

and the local density of states is given by

$$\rho_\sigma^i=-\frac{1}{\pi}\mathrm{Im}G_\sigma^i\ . \tag{2.14}$$

III. RESULTS AND DISCUSSION

In Figs. 2 and 3 we show results for the local density of states (LDS) in the DLM paramagnetic phase, i.e., $\eta=0$, for the ρ_2^0 model density of states. We show only the LDS at μ^- sites. The LDS at μ^+ sites is obtained by interchanging $\sigma\rightarrow-\sigma$. The parameters used are $U/W=0.7$ (W equals half of the bandwidth), $n=8.5$ electrons (Fig. 2), and $n=9.0$ electrons (Fig. 3). The self-consistent values for μ^+ $(=-\mu^-)$ are 1.44 and 0.94, respectively.

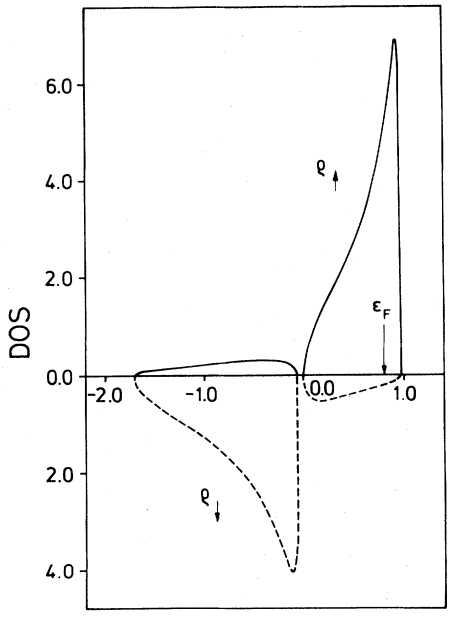

FIG. 2. Local density of states in the disordered magnetic moment phase ($\mu^+=-\mu^-$) at μ^- sites, using ρ_2^0. The parameters used are $U/W=0.7$ (W equals half of the bandwidth) and $n=8.5$ electrons. The LDS at μ^+ sites are obtained by interchanging $\sigma\rightarrow-\sigma$.

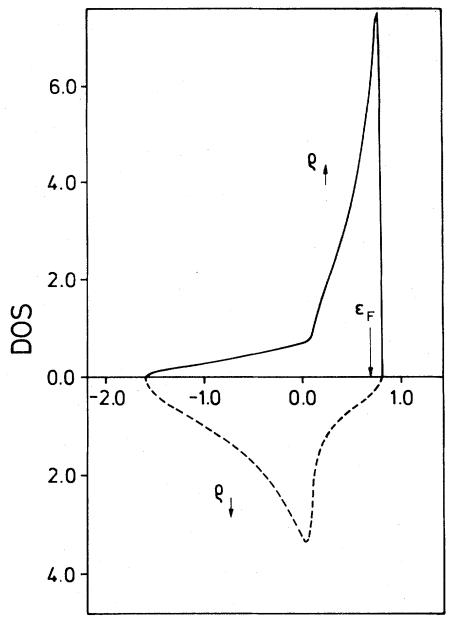

FIG. 3. Same parameters as in Fig. 2 are used and $n=9.0$ electrons.

In the former case, due to the large value of μ giving rise to a large exchange splitting, one obtains a gap in the LDS. In a more realistic calculation, one expects that the gap will disappear due to s-d hybridization. In all our results we took the energy units such that $W=1$.

Once the electronic structure is solved for a given set of parameters and for a given magnetic order η, the self-consistency must be carried out. This is done requiring that

$$\langle n_{i\sigma}\rangle=\int_{-\infty}^{E_F}d\omega\,\rho_\sigma^i(\omega) \tag{3.1}$$

and the values for $\langle n_{i\sigma}\rangle$ used in Eq. (2.5) are equal.

Our results concerning the phase diagram are shown in Figs. 4 and 5. The results using the elliptic density of states are displayed in Fig. 4, while those corresponding to the asymmetric density of states are shown in Fig. 5. In the phase diagram we show the Stoner condition

$$U\rho(E_F)=1 \tag{3.2}$$

by a solid line. Above this line, a ferromagnetic solution with $\eta=1$ is stable. We show also the condition for the existence of the DLM phase (dashed line),

$$UI(E_F)=1\ , \tag{3.3}$$

where

$$I(E_F)=-\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{E_F}(F^0)^2d\omega\ . \tag{3.4}$$

as also obtained previously.[6,13–15]

In Eq. (3.4), F^0 is the Green's function for a configuration with $\mu^+=\mu^-=0$. As discussed by Heine *et al.*,[6] above the boundary (3.3), there are self-consistent solutions for finite magnetic moments but in the disordered state. This condition holds for the instability towards the

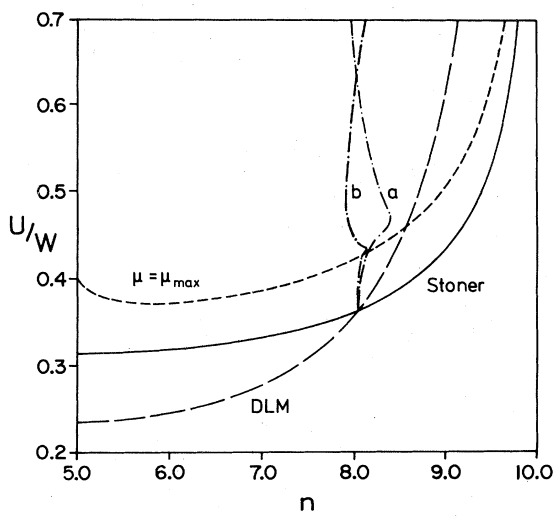

FIG. 4. Phase diagram using density of states ρ_1^0. The solid curve corresponds to the ferromagnetic-nonmagnetic boundary determined by the Stoner criterion, the short-dash curve to the boundary between saturated-nonsaturated ferromagnetic state, the long-dash curve to the paramagnetic-nonmagnetic boundary given by the criterion of Penn (Ref. 13), and the dashed-dotted curve to the boundary with respect to formation of single local magnetic moments in the ferromagnetic state. Here, *a* refers to global charge neutrality and *b* to local neutrality.

formation of a single local moment in a paramagnetic $\mu=0$ phase. The instability condition towards the formation of local moments has also been derived in the Gutzwiller model assuming a rectangular density of states.[7]

It is found that the condition for a DLM situation also holds for the case where we have equal number of magnetic moments pointing in both directions. This phase is physically equivalent to that originally described by Heine *et al.*[6]

The instability condition in this case is obtained from

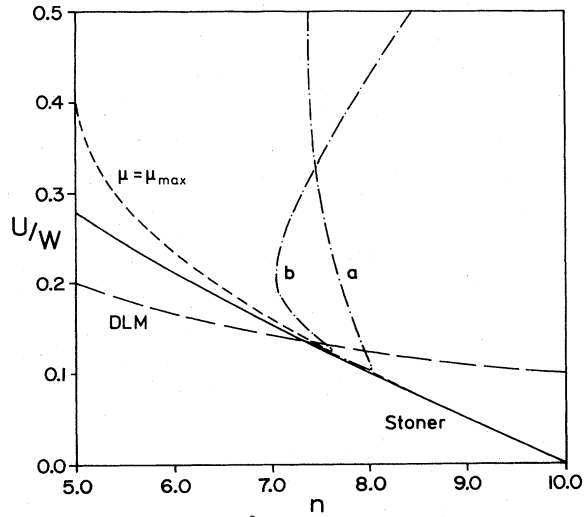

FIG. 5. Results for ρ_2^0. The same notation as in Fig. 4 is used.

$$d\mu_i=-\frac{1}{\pi}\mathrm{Im}\int_{-\infty}^{E_F}(dG_{\uparrow}^{i}-dG_{\downarrow}^{i})d\omega\ , \tag{3.5}$$

where G_{σ}^{i} is given by Eq. (2.13). Assuming now that $d\mu^{+}=-d\mu^{-}$ one obtains that

$$dG_{\uparrow(\downarrow)}^{+}=-(+)\tfrac{1}{2}U(F^0)^2d\mu^{+}\ . \tag{3.6}$$

An analogous expression can be written for $dG_{\uparrow(\downarrow)}^{-}$. Substituting Eq. (3.6) in Eq. (3.5) leads to the instability condition (3.3).

We also studied the instability assuming that $d\mu^{+}\neq d\mu^{-}$. Carrying out a calculation analogous to the one described above, we arrived at the equation

$$[1-U\rho(E_F)][1-UI(E_F)]=0\ , \tag{3.7}$$

which is the product of the Stoner and DLM conditions. This indicates that one can leave the nonmagnetic state continuously only by entering the ferromagnetic or the DLM phase. It is worth noting that the DLM condition is less dependent on the fine structure of the local density of states than the Stoner condition.[14]

We compared the energy of the DLM phase, $\eta=0$, and the ferromagnetic phase, $\eta=1$. Systems lying between the Stoner line (3.2) and the DLM boundary (3.3), on the right-hand side of their crossing, would be completely ordered at all temperatures, while those lying on the left-hand side would be disordered. The effect of temperature there is only to reduce the magnitude of the magnetic moments. However, the DLM phase might not be the configuration with lowest energy. It has been shown[16] that in this phase there are ferrimagnetic and antiferromagnetic solutions.

We investigated at $p_{+}=1$ the limiting behavior of μ^{-} viewed as an impurity in the vast collection of μ^{+} moments. In Figs. 4 and 5 we show by the dashed-dotted curve the boundary for the occurrence of $\mu^{-}\neq\mu^{+}$ at $p_{+}=1$. Clearly this instability with respect to local deviations for the homogeneous magnetization will depend on the boundary condition on the charge transfer between + and − sites. For this reason, the calculation was performed with a constant Fermi energy, and by allowing charge transfer and then by suppressing it via the introduction of an extra shift α of the electronic impurity level $\epsilon_0^{\mathrm{imp}}=\frac{1}{2}U(-\sigma\mu_{\mathrm{imp}}+n)+\alpha,\mu_{\mathrm{imp}}=\mu^{-}$, determined by the condition of local-charge neutrality.

In the phase called partially ordered PO, there are self-consistent solutions for values of the long-range-order parameter $\eta=1$ and $0\leq\eta\leq\eta_1$, where $\eta_1\leq 1$. The boundary for $\eta_1=1.0$ is shown. These systems would be completely ordered for $0\leq T\leq T_1$. At the temperature T_1, η jumps to η_1. Then, further increasing the temperature, one finds the system disorders following the normal magnetic transition.

Looking at Figs. 4 and 5, we see that the magnetic properties are extremely sensitive to the shape of the local density of states. Although the qualitative features are the same in the two cases, in order to apply the theory to a specific system it is necessary to have a realistic density of states.

If we assume that one of the two subbands e_g or t_{2g}, depending on the crystal symmetry, will lie in the range of

interest below the Fermi energy, it will suffice to take only one subband into account as a crude approximation. Then we must rescale the n axis in Figs. 4 and 5 to the corresponding occupation number in order to estimate the influence of subbands to our conclusions.

Figure 6 shows the local magnetic moments $\mu^{\pm}$ as a function of the concentration using the elliptic density of states. Note that for the case $n=8.0$, the solution $[\mu^{+}(p_{+}),\mu^{-}(p_{+})]$ starting with $\mu^{+}=-\mu^{-}$ at $p^{+}=0.5$ joins at a concentration $p_{+,0}<1$, another solution which is unfavorable because it has a higher energy for $0.5\leq p_{+}\leq p_{+0}$. The solution $\mu^{+}=\mu^{-}=\mu_{\mathrm{HF}}=2.0$ (HF represents Hartree-Fock) is valid for all p_{+} and is also shown. Notice that for $p_{+,0}<p_{+}<1$, μ_{HF} is the only solution. This behavior is typically found for high occupation numbers and indicates the breakdown of the alloy model because then there is no continuous solution between $p_{+}=0.5$ and $p_{+}=1$ except the trivial one μ_{HF}. The range of validity of the alloy model for magnetism is consequently given by the condition that this anomaly does not occur for $0.5\leq p_{+}\leq 1$. Figure 6 also shows that for Fe with $U=0.98$ eV, half-bandwidth $W=2.0$ eV, and occupation number $n=7.7$, the alloy model has continuous solutions for $\mu^{\pm}(p_{+})$. Within this framework the Curie temperature for Fe was found[5] to be $T_C=2250$ K. However, using the elliptic band and for parameters appropriate for Ni, $U=1.5$ eV, $W=3.0$ eV, and $n=9.5$ eV, the alloy model has no physical, i.e., no magnetic solutions at all in the whole range $0.5\leq p_{+}\leq 1$. This does not happen if one uses $\rho_2^0(\omega)$, which is more appropriate for fcc systems. For $p_{+}=0.5$ we obtain $\mu^{+}(0.5)=0.42$ resulting in $\mu^{+}(0.5)/\mu^{+}(1)=0.84$ as compared to 0.77 given by Hubbard.[3] We roughly estimate kT_C for Ni by taking the difference in energy of the phases characterized by $\mu^{+}(0.5)=-\mu^{-}(0.5)$ and $\mu^{+}(1)=\mu_{\mathrm{HF}}$, $\Delta^{E}=E(p_{+}=0.5)-E(p_{+}=1)$. Then we obtain $T_C=630$ K as compared with $T_C=1200$ K obtained recently by Hubbard.[3]

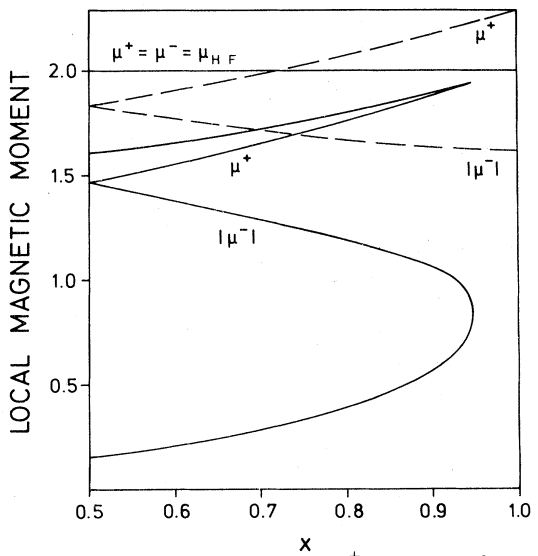

FIG. 6. Local magnetic moments $\mu^{\pm}$ in units of μ_B as a function of the concentration $x=p_{+}$ for an elliptic density of states and $U/W=0.49$ and assuming local-charge neutrality (shifting ϵ^{+}). Full curve corresponds to $n=8.0$ and dashed curve to $n=7.7$. μ_{HF} indicates the Hartree-Fock value of the moment.

That $kT_C\sim\Delta E$ can be seen by taking the simplest approximation for the free energy per atom

$$F=-\Delta E\eta^2+kT[p_{+}\ln p_{+}+(1-p_{+})\ln(1-p_{+})]\ , \tag{3.8}$$

where the spin entropy has been given by the configurational entropy resulting from the fictitious alloy. F can be expanded as

$$F=a\eta^2+b\eta^4+\cdots \tag{3.9}$$

and the Curie temperature T_C is given by the condition $a=0$ from where we obtain

$$kT_C=2\Delta E\ . \tag{3.10}$$

Note, a better treatment of the entropy would decrease the coefficient in front of ΔE in Eq. (3.10). Since a proper treatment of the magnetic entropy is still a major problem, in the following we use a factor of the order of 1 in order to estimate T_C.

In an Ising model the internal energy E is proportional to η^2. However, in our theory we are calculating E from the electronic parameters and the coefficient of η^2 near T_C is not ΔE but smaller.

Therefore, to estimate T_C we take $kT_C\approx\Delta E$, where the energy is given by

$$E(p_{+})=p_{+}\sum_{\sigma}-\frac{1}{\pi}\int^{E_F}d\omega\,\mathrm{Im}G_{i\sigma}^{+}(\omega)\omega$$
$$+(1-p_{+})\sum_{\sigma}-\frac{1}{\pi}\int^{E_F}d\omega\,\mathrm{Im}G_{i\sigma}^{-}(\omega)\omega-\cdots\ , \tag{3.11}$$

where ellipses indicate Hartree-Fock corrections.

The general behavior of T_C as a function of n is shown in Fig. 7 for the two densities of states $\rho_1^0(\omega)$ and $\rho_2^0(\omega)$. While T_C depends sensitively on W, U, and n, note that these parameters are determined from band-structure calculations and by fitting the magnetic moment at $T=0$. These results for T_C are 1 order of magnitude smaller than those predicted by the Stoner theory.

We may conclude that the alloy model for magnetism is valid only in that region of the phase diagram where at $p_{+}=0.5$ there is a solution with $\mu^{-}=-\mu^{+}$ and where at $p_{+}=1$ there is in the ferromagnetic phase a single local magnetic moment $\mu^{-}\neq\mu^{+}(p_{+}=1)$. This region in the phase diagram is bounded by the dashed-dotted curve on the right and by the Stoner criterion curve from below (see Figs. 4 and 5). By comparing Figs. 4 and 5, one sees that the difficulties encountered for cases $p_{+,0}<1$ are not density-of-states effects. For the density of states with the singularity at the high-energy edge, the situation is even worse, because the phase-diagram region in which the alloy model can be applied is more restricted. It would be interesting to extend the calculations of Heine *et al.*[6] and investigate the occurrence of $\mu_{\mathrm{impurity}}\neq\mu_{\mathrm{HF}}$.

There are qualitative arguments[17] for the existence of strong short-range order in itinerant magnetic systems. From our calculation we can confirm this statement at $T=0$. A single impurity in a homogeneous ferromagnet-

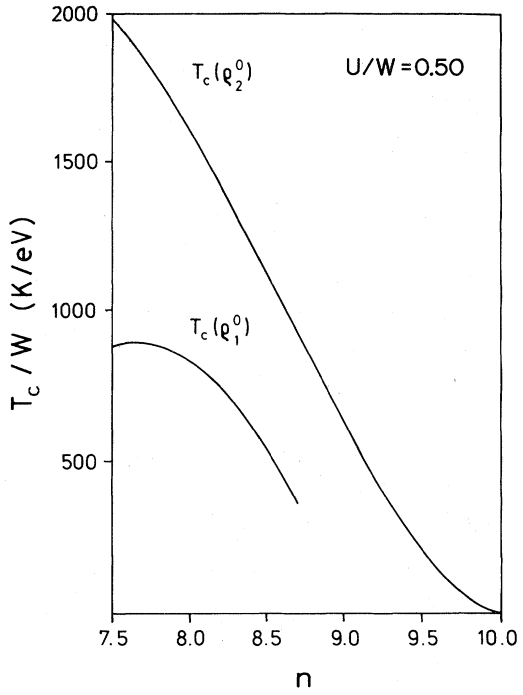

FIG. 7. The Curie temperature given by $T_C/W = [E(p_+=0.5) - E(p_+=1)]/kW$ as a function of n.

ic system means a strong local disturbance of the magnetic order and it tends to destroy the order in its vicinity. From Figs. 4 and 5 we see that there are large regions in the phase diagram where a single μ^- cannot exist in a uniform collection of μ^+ moments.

The validity of the alloy model for magnetism in transition metals is thus not so much limited by the choice of the electronic density of states as it is by the improper handling of the distribution function for the local magnetic moments. The typical results of $\mu^{\pm}(p_+)$ shown in Fig. 6 mean simply that $\mu_i(p_+, \mu_{NN}, \dots)$ has not always a solution if we approximate the magnetic moments μ_{NN} of the nearest neighbors to i by only μ^+ or μ^-. However, solutions will still exist if one allows a distribution of the μ_{NN} determined by $p(\mu) \sim \exp[-\beta \cdot \Delta E(\mu)]$. Here, $\Delta E(\mu)$ is the energy of the moment μ embedded in a medium with a magnetic moment $\bar{\mu}$.

In the alloy model the moment distribution is given by a linear combination of two delta functions whose weights are given for all temperatures by p_+ and p_- and whose positions are determined by the self-consistent values of $\mu^{\pm}$. In contrast, in the theory of magnetism in transition metals by Hubbard[1-3] and Hasegawa[4] the distribution function of the moments, i.e., of the exchange fields, is included. Thus difficulties described in this paper do not appear in those treatments.

The mean value of the local moment, i.e., the magnetization of the homogeneous magnetic medium, attains the Hartree-Fock value at $T=0$, at least for high occupation numbers,[4] due to the very definition of the distribution function used by Hubbard. This implies that the existence of a magnetic Hartree-Fock ground state is sufficient to make the theory valid at all temperatures.

It might be interesting to study whether the validity of the alloy model may be extended by corrections to the Hartree-Fock approximation including the most important fluctuations of the magnetic moments. From the local Green's function $g_i^{\sigma}(\epsilon) = 1/(\epsilon - \alpha_{\sigma})$, where $\alpha_{\sigma} = -\sigma(U/2)\mu_i$, one finds with the help of the decoupling procedure of Hasegawa[18] for the average Green's function, dropping the spin index now,

$$\langle g_i \rangle = \tfrac{1}{2}\left[1 + \frac{\langle \alpha \rangle}{(\langle \alpha^2 \rangle)^{1/2}}\right] \frac{1}{\omega - (\langle \alpha^2 \rangle)^{1/2}} + \tfrac{1}{2}\left[1 - \frac{\langle \alpha \rangle}{(\langle \alpha^2 \rangle)^{1/2}}\right] \frac{1}{\omega + (\langle \alpha^2 \rangle)^{1/2}} . \quad (3.12)$$

This corresponds to an alloy with concentration $\tilde{p}_+ = \frac{1}{2} \cdot \{1 + [\langle \alpha \rangle / (\langle \alpha^2 \rangle)^{1/2}]\}$ and $\tilde{p}_- = 1 - \tilde{p}_+$ of atoms with levels $\tilde{\epsilon}_{\pm} = \pm (\langle \alpha^2 \rangle)^{1/2}$. By using this scheme, the system can be regarded as an alloy again. Now, the alloy's energy levels $\tilde{\epsilon}_{\pm}$ are not determined self-consistently corresponding to Eq. (3.1), a procedure which was shown to fail in some cases; instead, they are determined as averages via $p(\mu)$ just as the concentration $\tilde{p}_+$. Here $p(\mu)$ is governed by the energy of the moment embedded in the alloy. This extended version of alloy theory could be used for treating magnetism also in Ni and alloys thereof.

The applicability of the simple-alloy model is related to the occurrence of a double-peak structure in the distribution function $p(\mu)$, of course. A minimum in $\Delta E(\mu)$ corresponds to a maximum in $p(\mu)$ and vice versa. Then, having three extrema in $\Delta E(\mu)$ at $\mu_i, i = 1,2,3$ means that for a medium with moments $\bar{\mu}(T)$ there are three self-consistent single-impurity solutions μ_i. On the other hand, the new boundary, shown in Figs. 4 and 5, is determined by the condition that at $T=0$, respectively at $p_+ = 1$, two single-impurity solutions coincide. This corresponds to a situation with $\bar{\mu}(0) = \mu_{HF}$ and $\mu_1 = \mu_2$ only giving rise to a single dip in $\Delta E(\mu)$ at $\mu_3 = \mu_{HF}$. A double-peak structure of $p(\mu)$, triggered by two dips in $\Delta E(\mu)$, cannot be seen at $T=0$ but for $T \gtrsim 0$.

In summary, the alloy model is useful since calculations in its framework are relatively simple and it permits the formulation and calculation of important magnetic properties such as short-range spin correlations and entropy in a physically transparent manner. Furthermore, extensions to study magnetism in alloys and magnetic impurities are straightforward. Its limitations are as follows: (i) The alloy model can be used if the lifetime of the fictitious alloy components is longer than the hopping time, i.e., if the distribution of magnetic moments is well centered around μ^+ and μ^-. (ii) The alloy model is valid in the region of the phase diagram where solutions in the range $0.5 \leq p_+ \leq 1.0$ can be obtained. (iii) The validity of the alloy model is limited by the simple moment distribution consisting of a linear combination of two delta functions. An improvement to the simple alloy model was discussed—how to take into account a distribution of local moments going beyond the Hartree-Fock approximation. Obviously, we are still far from understanding the

puzzling magnetic properties of transition metals and many more studies of these materials must be performed.

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APPENDIX

The homogeneous medium, $p_+ = 1$, is described by the Green's function

$$F^\sigma(\omega) = F^0(\omega - \epsilon_m^\sigma) ,$$

with

$$\epsilon_m^\pm = \tfrac{1}{2} U(\mp\bar{\mu} + \bar{n}) .$$

The impurity Green's function is given by

$$G_i^\sigma(\omega) = F^\sigma(\omega)/[1 - (\epsilon_i^\sigma - \epsilon_m^\sigma)F^\sigma(\omega)] ,$$

with

$$\epsilon_i^\pm = U n_i^\mp .$$

The impurity occupation numbers $n_i^\pm$ are determined then by the equations

$$f = n_i^+ - \left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega \, G_i^+(\omega) = 0 ,$$

$$g = n_i^- - \left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega \, G_i^-(\omega) = 0 ,$$

where E_F is the Fermi energy of the medium.

The condition for the coincidence of two solutions n_i^+, n_i^- is fulfilled when both curves touch each other. This can be expressed as[19]

$$\frac{\partial f}{\partial n_i^+} \Big/ \frac{\partial f}{\partial n_i^-} = \frac{\partial g}{\partial n_i^+} \Big/ \frac{\partial g}{\partial n_i^-}$$

resulting in

$$1 = U^2 \left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega [G_i^+(\omega)]^2 \times \left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega [G_i^-(\omega)]^2 ,$$

which gives the new boundary $U/W(n)$ for the case of global charge neutrality.

The equivalent condition for local charge neutrality is achieved by introducing a shift α to the local impurity potential which is determined by $n_i = \bar{n}$

$$\epsilon_i^\pm = \tfrac{1}{2} U(\mp\mu_i + \bar{n}) + \alpha .$$

The equations for μ_i and α are given now by

$$f = \mu_i - \left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega [G_i^+(\omega) - G_i^-(\omega)] = 0 ,$$

$$g = \bar{n} - \left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega [G_1^+(\omega) + G_i^-(\omega)] = 0 .$$

Using the same arguments as before, we obtain

$$1 = -U \frac{\left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega [G_i^+(\omega)]^2 \left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{\epsilon_F} d\omega [G_i^-(\omega)]^2}{\frac{1}{2}\left[-\frac{1}{\pi}\right] \mathrm{Im} \int^{E_F} d\omega \{[G_i^+(\omega)]^2 + [G_i^-(\omega)]^2\}} .$$

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