PHYSICAL REVIEW B VOLUME 41, NUMBER 10 1 APRIL 1990

Stoner exchange interaction in transition metals

Gernot Stollhoff, Andrzej M. Oleś,* and Volker Heine†
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

(Received 17 January 1989; revised manuscript received 20 November 1989)

The theory of magnetism in transition metals is often expressed in terms of a Stoner exchange parameter I. Results for I are presented from electronic-structure calculations with correlations for a d-band-only Hubbard type of Hamiltonian. The main effects are: (a) Due to correlation, I depends substantially on the volume via the bandwidth. (b) There are analogous corrections to lattice constants calculated with the local-density approximation (LDA). (c) I also depends on magnetization, band filling, and crystal structure. (d) In Ni the reduction of charge and spin fluctuations almost eliminates the contribution to I of exchange between different orbitals. (e) I computed in the LDA is usually overestimated by 10%–20% because the LDA largely neglects spin correlations.

I. INTRODUCTION

In the theory of magnetism in transition metals and their alloys it is common to involve a "Stoner parameter" I (Refs. 1 and 2) to represent the exchange interaction between d electrons. The band structures of the simple ferromagnetic transition metals have been calculated many times,[3–6] for example with the local spin-density approximation (LDA) (Refs. 7–10) for exchange and correlation. It is well known that, except for small deviations in the case of Ni, the bands can be fitted quite well by a tight-binding (TB) model with a more or less constant exchange splitting of the d bands by an amount

$$\Delta = IM \ , \tag{1.1}$$

where M is the magnetic moment in Bohr magnetons per atom.[4,11] This defines I.

An alternative definition of I is to separate the LDA ground state energy into the following contributions:

$$E(M_0)=E(0)+\tfrac{1}{4}\int_0^{M_0^2} D(M)dM^2-\tfrac{1}{4}IM_0^2 \ , \tag{1.2}$$

where $E(0)$ is the energy of the nonmagnetic state and the second term describes the increase in kinetic energy due to occupying progressively higher band states within the majority band. The last term describes the gain in interaction energy due to the (ferro)magnetic order. Experience shows that the LDA in such calculations does not lead to any sizable dependence of I on the degree of magnetic polarization M.[12,13] The largest deviation found so far to our knowledge occurred in the case of fcc Fe, where I decreased by 4% with the magnetization rising to the maximal value.[14] Since the ground state magnetic moment comes out well in LDA, the value of I as obtained by LDA compares almost perfectly with I as defined in (1.1). Moreover, I is essentially independent of the nature of the magnetic order, ferro- and antiferromagnetic calculations giving very similar values of I.[15] Since the d-electron density is rather small at the edge of the Wigner-Seitz cell, it is supposed from the spirit of the calculations that I is an intra-atomic constant, always the same for the given element in any alloy or magnetic configuration. Furthermore, I does not show any sizable volume dependence. These findings naturally suggest treating all magnetic problems in itinerant magnetism within a conventional one-particle tight-binding picture with the additional exchange energy

$$E_{\text{xc}} = -\tfrac{1}{4}IM^2 \ , \tag{1.3}$$

where I is usually taken as the LDA value but need not be. This Hamiltonian, although formally equivalent to a Hubbard model, is to be treated strictly within the one-particle approximation and all correlation effects are assumed to be included in the effective parameter I. That maps it onto the philosophy of spin density functional theory, applied within a tight-binding framework. We believe this is the most general and modern way to view the status of the conventional one-electron Stoner picture with a constant parameter I. For more details about these theories we refer to Refs. 16–18.

Two broad questions now arise:

(a) Can different magnetic properties all be fitted by a single constant I (for a given element) in different crystal structures, magnetic configurations, and alloys?

(b) How good is the I obtained from the LDA?

We have done calculations on a Hubbard-type Hamiltonian, which threw light on both these questions. The model is restricted for simplicity to five d bands only with an overall bandwidth W, with a so-called on-site Coulomb interaction U, and exchange interactions J and ΔJ. As usual, we suppose that U and J are screened interactions, screened by the s and p electrons and by correlations at shorter than atomic distances with high virtual excitation energies. We assume that all these screening effects are independent of the environment, confining ourselves to modest changes of volume. We obtained the correlated ground state of this Hamiltonian by starting from the self-consistent (SCF) ground state and including correlation effects variationally within the local ansatz,[19–21] which for this model system can be seen as a generalized Gutzwiller ansatz.[22] Thus our model investigates the effect of the correlations and screening originating in the d band itself. We further restrict ourselves to those correlations described by operators on single atoms only. These we call atomic correlations in the following. Details will be given in Sec. II.

We restrict our calculation to the nonmagnetic state and to states (also correlated) originating from ferromagnetic SCF states with a given moment M obtained within a rigid-band model. The basic output of the calculations in the energy of the correlated ground states $E_0(M)$. The effective Stoner parameter I is extracted from our calculation in a similar way to what was done for the LDA in (1.2). The total energy is again separated into three parts,

$$E_0(M_0)=E_0(0)+\tfrac{1}{4}\int_0^{M_0^2} D(M)dM^2-\tfrac{1}{4}\int_0^{M_0^2} I(M)dM^2 , \tag{1.4}$$

where $E_0(0)$ is the energy of the correlated nonmagnetic state. The second part describes the increase in kinetic energy of the uncorrelated magnetic state and is exactly the same as in the LDA expression before (1.2). The final term includes all interaction and correlation effects. This Stoner parameter is introduced and discussed in detail in Sec. III.

Equation (1.4) defines $I(M)$ as a function of M which is extracted in practice by numerically differentiating $E_0(M)$. We find that $I(M)$ does indeed vary with M, in contrast to the situation with the LDA when taking I as a constant in (1.2) was a good approximation. It should be noted that the middle term in (1.4) is purely the one-electron band energy: Additional kinetic energy is needed to produce correlations, as is clear from the uncertainty principle, and this is all incorporated in $I(M)$. The bandwidth W is taken from LDA calculations and the ratio U/W is so chosen that the ground state has the proper magnetic moment M_0. This fixes $I(M_0)$ so that it is by definition equal to the value one would use in a d-band model derived from LDA.

Our main conclusion regarding question (a) above is that I is indeed dependent on volume. This volume dependence does not show up directly here but arises through the dependence of I on the bandwidth W. Without correlations I would be independent of W: For a fivefold d-band system in a certain degeneracy limit (Sec. II) we have that $I_{\mathrm{SCF}}=I_0$ with (ignoring ΔJ)

$$I_0=\tfrac{1}{5}(U+6J) . \tag{1.5}$$

However, correlations change this substantially. As already mentioned, $I(M)$ contains the change of kinetic energy due to correlations and $I(M)$ therefore has to depend on W. This can be seen from Fig. 1. It is convenient to express $I(M)$ dimensionlessly in terms of

$$\bar{I}(M)=I(M)/I_0 . \tag{1.6}$$

Figure 1 plots $\bar{I}(0)$ as a function of band occupation for bcc and fcc d bands for different ratios U/W. As can be seen, $I(0)$ decreases considerably with increasing U/W: The narrower the band, the easier it is for electrons to correlate and hence the more screened is the exchange interaction. Incidentally, the fact that $\bar{I}(0)$ in Fig. 1 depends on the band filling for $U/W=0$ contrary to (1.5) results from anisotropic occupations of the e_g and t_{2g} partial states and might be to some extent caused by the rigid-band ansatz made in the one-electron part of our calculation.

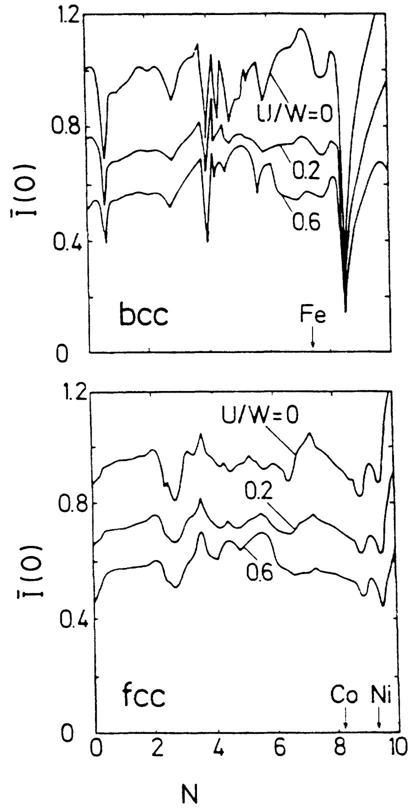

FIG. 1. Normalized Stoner parameter $I(0)$ for canonical bcc and fcc densities of states for $U/W=0$ (i.e., in SCF approximation), 0.2 and 0.6.

Furthermore, it will be shown that I depends on the magnetization M, too. This arises from a specific part of the correlations, namely what we call the Hund's rule or spin correlations on individual atoms.[19-21] These are important in the nonmagnetic case, but are dramatically changed in going to the magnetic states, particularly the saturated state ($M=M_s$) with majority band completely full. The latter takes no part in the atomic correlations, so that there are only correlations within the minority carriers and one automatically has full Hund's-rule coupling. This reduces $I(0)$ by typically 20% relative to $I(M_S)$.

Let us now turn to part (b) of our question. It is not obvious why our work has anything to say about LDA. The LDA works with approximations which are completely different from the ones used here. However, the dependence of I on M and on V which we obtained could be explained quite simply. A next natural step is therefore to find a reason why these dependences are lacking in the LDA, and, furthermore, to give quantitative estimates for these shortcomings of the LDA. As mentioned above, the dependence of I on M originates from atomic spin correlations and we know, from calculations on atoms and small molecules, that such spin correlations are not well treated in LDA. For a spin-unpolarized atomic calculation one obtains only the weighted average energy over all possible spin configurations for a given electron density. It is only by explicitly breaking the spin symmetry that one can include the Hund's-rule effect. A spin-unpolarized LDA calculation for a solid is therefore expected to have no spin correlations included either. We will elaborate on this in more detail below. This defect of LDA can be simulated within our computations by switching off spin correlations. Without such correlations, the dependence of I on M in our calculations is in fact strongly reduced. We believe the same effect explains the constancy of $I(M)$ in LDA, which points to the lack of spin correlations as a specific defect of LDA. We will discuss the magnetization dependence of I and the corresponding LDA results in Sec. IV,

We turn now to the volume dependence of I which in our calculations comes via the atomic correlations which in turn involve the kinetic energies within a rather narrow d band, as already discussed. However, these correlations are in LDA approximated by those of the homogeneous electron gas with the high $3d$-electron density. Moreover, they are relatively independent of volume because the d-electron density depends little on volume. The correlation hole within a homogeneous system of the d-orbital density is so small that within this approximation the d-orbital fluctuations are almost completely screened within the atom itself,[12] making atomic correlations useless. Thus, LDA underestimates atomic correlations, but we know that these are strong from full *ab initio* many-body calculations on other materials with nonuniform electron density, namely semiconductors.[23,24] There, it turned out that even for not too inhomogeneous systems atomic correlations really are of considerable importance and are not sizably decreased by shorter range correlations. Thus we are able to make statements about the deficiencies of LDA from including and excluding the various effects of our correlation treatment within our model Hamiltonian and even to make some semiquantitative estimates of the corrections. The volume dependence of I is treated in Sec. V.

The volume dependence of I contributes directly to the magnetic pressure and hence to the magnetovolume effect. While in LDA the magnetic pressure arises predominantly from the kinetic energy of the one-electron d states, here the volume dependence of I due to correlation corrections to the kinetic energy contributes to the magnetic pressure as well. As can be seen from Fig. 1, these contributions are not negligible. Various aspects of the magnetovolume effect will be discussed in Sec. VI as well as the corrections to equilibrium atomic volumes calculated by LDA.

Within this paper we will restrict ourselves to the ferromagnetic Stoner parameter I_F. We expect that an antiferromagnetic Stoner parameter I_{AF} behaves similarly. The situation for a disordered local moment state is more complicated but will not be covered in this paper.

Finally it should be mentioned that the present study into the nature of I, starting from a Hamiltonian with on-site interactions, follows a long tradition. Such work started with Wohlfarth,[25] who even already discussed the magnetization dependences of I within the SCF approximation. Later, Kanamori[26] and Edwards[27] included many-body corrections for Hubbard models. In particular, the dependence of I on M (Ref. 27) and on V (Refs. 28 and 29) due to these many-body effects were treated. Preliminary results of our own investigations have been published before.[30–32] A comparison of our many-body treatment with other methods,[28,33–37] that have been developed before but cannot be applied here for various reasons, is given elsewhere.[38]

II. THE MODEL AND ITS TREATMENT

Although *ab initio* correlation calculations for solids are feasible,[23,24] performing such computations for the transition metals is still some way into the future. At present we will restrict ourselves to a model Hamiltonian which describes the dominant features of the electronic states within $3d$ transition metals. It is a generalized Hubbard Hamiltonian, which gives a qualitatively satisfying description of the delocalized d electrons, as well as their atomic interaction in the transition metals. It consists of two parts,

$$H=H_0+H_1 \ , \tag{2.1}$$

$$H_0=\sum_{\nu\sigma\mathbf{k}} \varepsilon_\nu(\mathbf{k})n_{\nu\sigma}(\mathbf{k}) \ , \tag{2.2}$$

$$\begin{aligned}H_I=\tfrac{1}{2}\sum_{\substack{lij\\ \sigma\sigma'}} \{ & U_{ij}a_{i\sigma}^\dagger(l)a_{j\sigma'}^\dagger(l)a_{j\sigma'}(l)a_{i\sigma}(l)\\ & +J_{ij}[a_{i\sigma}^\dagger(l)a_{j\sigma'}^\dagger(l)a_{i\sigma'}(l)a_{j\sigma}(l)\\ & +a_{i\sigma}^\dagger(l)a_{i\sigma'}^\dagger(l)a_{j\sigma'}(l)a_{j\sigma}(l)]\} \ .\end{aligned} \tag{2.3}$$

Here H_0 describes the one-particle or band behavior of the d electrons and we refer to it loosely as the kinetic energy. The $\varepsilon_\nu(\mathbf{k})$ denote the canonical d-band energies[39] and $n_{\nu\sigma}(\mathbf{k})$ the corresponding electron number operators for the relevant crystal structure (i.e., bcc or fcc). The total bandwidth W is the only adjustable parameter in H_0, with the values 5.43, 4.84, and 4.35 eV for Fe, Co, and Ni, respectively.[40] The $\varepsilon_\nu(k)$ denote energies with respect to the center of the bands, so that our "kinetic" energy is always negative. Our H_I describes the atomic interactions between local states i and j on atom l which are of t_{2g} and e_g symmetry, with corresponding creation operators $a_{i\sigma}^\dagger(l)$. The interaction matrix elements U_{ij} and J_{ij} are expressed in terms of U, J, ΔJ (Ref. 37) as shown in Table I of Ref. 20. The dominant terms come from the Coulomb interaction U with further contributions from the exchange term J and its anisotropy ΔJ. The anisotropy is fixed at its atomic ratio, $\Delta J=0.15J$, while for J/U we take a constant ratio of 0.2 for most of our calculations. We will discuss below whether our results depend crucially on this ratio. By fixing the ratios $\Delta J/J$ and J/U we have reduced H_1 to only one adjustable parameter U. Note that hybridization effects with s electrons are neglected. Within this model they just lead to noninteger band occupation and a strongly screened effective U.

Typically we have that $W \simeq 5$ eV and $U < 0.8W$.[19,21] As specific values for Fe, Co, and Ni, we take the LDA values of $W = 5.43$, 4.84, and 4.35 eV, respectively.[40]

The one-particle ground state $|\phi_0\rangle$ of H_0 is the usual Slater determinant easily computed from $\varepsilon_\nu(\mathbf{k})$. Correlations are then included within the local ansatz for the correlated wave function $|\psi_0\rangle$.[41,42] Here they are restricted to local operators $O_n(l)$ which act on one site l only. The correlated state $|\psi_0\rangle$ has the form

$$|\psi_0\rangle = \exp(S)|\phi_0\rangle = \exp\left[-\sum_{l,n}\eta_n O_n(l)\right]|\phi_0\rangle \; . \tag{2.4}$$

The η_n are variational parameters which are obtained by a minimization of the ground state energy

$$E_0 = \frac{\langle\psi_0|H|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \; . \tag{2.5}$$

Three different forms have been chosen for the local operators $O_n(l)$, namely

$$\begin{aligned} O_i^{(1)}(l) &= n_{i\uparrow}(l)n_{i\downarrow}(l) \; , \\ O_{ij}^{(2)}(l) &= \sum_{\sigma\sigma'} n_{i\sigma}(l)n_{j\sigma'}(l) \; , \\ O_{ij}^{(3)}(l) &= \mathbf{S}_i(l)\mathbf{S}_j(l) \; , \end{aligned} \tag{2.6}$$

where i and j are the basis orbitals. The first kind reduces charge fluctuations within an orbital i and the second between different orbitals i and j. The third kind allows for Hund's-rule coupling of the delocalized electrons, i.e., it describes spin correlations between electrons, when they occupy the same site. Actually, this variational calculation is not performed exactly. Instead a variational expansion of the correlation energy up to second order in η_n is made. The restriction of the correlations to atomic operators leads to deviation from the exact treatment of (2.1) by typically 5%. For the ratio U/W considered here, the errors due to the variational expansion are of the order of one up to a few percent.[19] For further details of the calculations, see Refs. 19 and 21.

The ansatz (2.4) is generalized to ferromagnetic states in the following way. In a ferromagnetic case, a one-particle state $|\phi_0(M)\rangle$ is constructed in the normal way with the eigenstates of H_0 for the majority spin component bands filled up to the energy $E_F + \Delta_1$, while those in the minority band are only filled up to the energy $E_F - \Delta_2$, where E_F stands for the Fermi energy in the nonmagnetic case. This means that a rigid-band approximation is made, i.e., it is assumed that the one-particle band structure $\varepsilon_\nu(\mathbf{k})$ in (2.2) for each band does not change with magnetization. We then have

$$\int_{E_F}^{E_F+\Delta_1} n(E)dE = \int_{E_F-\Delta_2}^{E_F} n(E)dE = \frac{M}{2} \; , \tag{2.7}$$

where $n(E)$ is the total density of states per spin corresponding to $\varepsilon_\nu(\mathbf{k})$. This ferromagnetic state $|\phi_0(M)\rangle$ is then correlated in the same way (2.4) as the nonmagnetic state $|\phi_0\rangle$.[20,21] The total energy $E_0(M)$ of the correlated ferromagnetic state with moment M is computed in the same fashion as that of the nonmagnetic state before [Eqs. (2.4) and (2.5)]. For specific ferromagnetic metals, the interaction parameters U are chosen so that the ground state is the state with the experimental magnetic moment M_e. For Fe, Co, and Ni it turns out that the outcoming interaction is in very good agreement with effective interactions derived from gas phase spectroscopy.[43] For a detailed discussion, we refer to Appendix A. This agreement indicates that the model Hamiltonian chosen here offers a fair description of the d electrons.

III. THE STONER PARAMETER

Having defined the Hamiltonian and the ground states for different magnetization M, it is straightforward to define the Stoner parameter $I(M)$ from the energy $E_0(M)$ of the correlated ground state, as given by Eq. (1.4). The Stoner criterion for ferromagnetism is written as

$$D(0) \le I(0) \; , \tag{3.1}$$

where

$$D(0) = 1/n(E_F) \; . \tag{3.2}$$

The magnetic ground state and its moment M_0 are then given by the equilibrium condition

$$D(M_0) = I(M_0) \; , \tag{3.3}$$

when there is a free Fermi level in both the majority and minority bands, which we shall refer to as the case of "weak" ferromagnetism. The function $D(M)$ with our rigid-band ansatz (2.1) is directly obtained as a function of $n(E)$:

$$D(M) = \frac{1}{M}[\Delta_1(M) + \Delta_2(M)] \; , \tag{3.4}$$

with Δ_1 and Δ_2 defined by Eq. (2.7). Note that $D(M)$ is a constant for a constant density of states. In fact it is only the second derivative of $n(E)$ which leads to an explicit dependence of $D(M)$ on M. The function $I(M)$ cannot be given analytically but is obtained by a numerical calculation of $E_0(M)$ for different M as described in Ref. 21 and a subsequent separation via Eq. (1.8). This function needs to be calculated for different numbers of d electrons and for specific ratios of U/W. In the case of "strong" magnetism the majority band is completely filled, the moment M_s is fixed by the number of electrons, and we can only say that $I(M_s)$ is greater than some minimum value needed to fill the majority band completely [which is $D(M_s)$]. Incidently, the $I(M)$ can be given a physical meaning even for M not equal to the equilibrium value M_0, because one can imagine a (very large) magnetic field applied such as to stabilize M at any given value.

Next, we investigate the question to what extent I does indeed depend on band occupation, on details of the different interactions, and finally on the magnetic moment due to our complete treatment of correlation and exchange. In the next sections we will investigate first the effects of exchange and then the dependence on band filling and on different interaction parameters.

A. Analytic calculations within one-particle approximation

While the computation of $I(M)$ for the correlated ground state is performed numerically, analytic computations may be performed on the one-particle (Hartree-Fock) level. By them, it may be demonstrated explicitly how the Stoner parameter depends on details of band filling. The Stoner parameter I_{SCF} in Hartree-Fock (HF) approximation is derived simply from the expectation value of the interaction part of the model Hamiltonian, when assuming the rigid-band approximation. It is given as

$$\begin{aligned} E_{\mathrm{int}} = & (U+2J)\sum_{i} n_{i\uparrow}n_{i\downarrow} + (U+2J)\sum_{i<j} n_i n_j \\ & -3\sum_{ij} J_{ij}(n_{i\uparrow}n_{j\uparrow}+n_{i\downarrow}n_{j\downarrow}) \\ & -2\sum_{i<j} J_{ij}(n_{i\uparrow}n_{j\downarrow}+n_{i\downarrow}n_{j\uparrow}) \ , \end{aligned} \tag{3.5}$$

where $n_{i\sigma}$ are the expectation values for the occupation of orbital i with spin σ and $n_i = n_{i\uparrow}+n_{i\downarrow}$.

For simplicity we ignore below the terms proportional to ΔJ. Then it follows that

$$I_{\mathrm{SCF}}(0) = \frac{1}{m}[(U+2J)+(m-1)J] \ , \tag{3.6a}$$

$$I_{\mathrm{SCF}}(0) = \frac{1}{m}(U+J)+J \ , \tag{3.6b}$$

when the density of states at the Fermi energy is constant and splits equally among m different orbitals. If the total density of states is not equally split, then we have instead

$$I_{\mathrm{SCF}}(0) = \alpha(U+J)+J \ , \tag{3.7a}$$

with

$$\alpha = \sum_{i=1}^{m} n_i^2(E_F)/n^2(E_F) \ , \tag{3.7b}$$

where the $n_i(E)$ are the m partial densities of states.

In our specific application we have $m=5$ and that the density of states is always split into a two-dimensional e_g and a three-dimensional t_{2g} contribution, so that the smallest value of α equals $\frac{1}{5}$, the largest $\frac{1}{2}$. When including ΔJ and writing for the two types of orbitals

$$\begin{aligned} n_{t_{2g}}(E_F) &= \tfrac{1}{5}n(E_F)(1-2s) \ , \\ n_{e_g}(E_F) &= \tfrac{1}{5}n(E_F)(1+3s) \ , \end{aligned} \tag{3.8}$$

we obtain

$$I_{\mathrm{SCF}}(0) = \tfrac{1}{5}(U+J-4\Delta J)+J+\tfrac{6}{5}(U+J+\tfrac{7}{2}\Delta J)s^2 \ . \tag{3.9}$$

Thus without orbital asymmetry ($s=0$), ΔJ reduces $I_{\mathrm{SCF}}(0)$ by $-0.12J$ or roughly 10% if we take $\Delta J = 0.15J$. Assuming constant and equal partial densities of states at the Fermi level leads to this isotropic value of $I_{\mathrm{SCF}}(0)$ as a lower limit for the Stoner parameter, and any unequal occupation ($s \neq 0$) of the different orbitals increases it. This leads to a variation of the Stoner parameter $I(M)$ as a function of magnetization since s will in general vary with the degree of band polarization. Allowing for the density of states to vary with E at the Fermi energy leads to additional corrections ΔI if and only if the partial occupancies of the different orbitals n_i are different. They are proportional to both these modifications

$$\Delta I_{\mathrm{SCF}}(0) = \sum_{ij} \alpha_{ij}\Delta n_i \left.\frac{\partial n_j(E)}{\partial E}\right|_{E=E_F} \ , \tag{3.10a}$$

with

$$\Delta n_i = n_i - \bar{n} \ , \tag{3.10b}$$

where $\bar{n}$ is the average occupation per orbital of each site. The corrections are different for the term proportional to J in Eq. (3.7) as compared with those in the term $(U+J)$. This form of ΔI guarantees that in the case $\Delta n_i = 0$, i.e., in the degenerate band limit, the details of the density of states do not enter the Stoner parameter which then is of the form (3.5). Neither the terms α_{ij} nor the corrections due to correlations will be discussed analytically. All these discussions already indicate that in general even the interaction contributions to $I(M)$ alone already cause it to be a general function of magnetization as written in (1.4).

B. Detailed results for $I(0)$

Next, we discuss the dependence of $I(0)$ on band filling (i.e., number of electrons N per atom) and different ratios U/W and I/U, and different crystal structures. Moreover, by switching off some or all of the correlation operators in (2.6) and varying the parameters in H_1 (2.3) we can get insight into the origin of some of the effects found.

We start by varying the ratio U/W and the degree of band filling N with constant $J/U=0.2$ and $\Delta J/J=0.15$. The normalized $I(0)$ (1.6) is shown in Fig. 1 for the bcc and the fcc structures as a function of N for several values of U/W. The limit $U/W \to 0$ corresponds to the uncorrelated HF state and is calculated with finite U but switching off all correlation in (2.4). We note first that $I(0)$ is a decreasing (in fact monotonically decreasing) function of U/W. This is because correlation keeps electrons apart and hence reduces ("screens") their exchange interaction. Another perspective is to note that the electrons have the greatest freedom to correlate between up and down spin bands in the unmagnetized state, which gets reduced in a magnetized state and disappears in the limit of a full majority band. (In that limit the only remaining correlation is among minority spin electrons.) Thus the energy of the magnetized state is higher relative to the unmagnetized one with correlations than without, which translates according to (1.4) into a smaller $I(M)$. Secondly, we note in the upper part of Fig. 1 considerable variation of $I(0)$ with N. Most of this variation is already present for $U/W=0$ and originates from unequal occupation of the orbitals, as discussed in connection with (3.6)–(3.8). Typically, $I(0)$ for $U=0$ is above 0.9, the value obtained, when all orbitals have the same partial densities of states at E_F [Eqs. (3.6) and (3.9)]. This is most evident for $N \to 10$ in both structures and generally

TABLE I. Normalized Stoner parameter in the HF approximation $[5I_{\mathrm{SCF}}(0)/(U+6J)]$ and with correlations involved $[5I(0)/(U+6J)]$, the values of $I(0)/I(M_0)$ and the ratio $I_2(0)/I(0)$ explained in the text) for bcc Fe ($N=7.4$) for different pairs of (U,J) which give the same $I(M_0)$.

J/U	U/W	$5I_{\mathrm{SCF}}(0)(U+6J)$	$5I(0)/(U+6J)$	$I(0)/I(M_0)$	$I_2(0)/I(0)$
0.1	0.606	1.089	0.659	1.110	1.091
0.15	0.496	1.073	0.656	1.074	1.113
0.2	0.420	1.060	0.656	1.055	1.126
0.25	0.363	1.049	0.660	1.043	1.133
0.3	0.320	1.041	0.666	1.037	1.136
0.4	0.257	1.030	0.678	1.031	1.138

plays a bigger role for bcc than for fcc. However, there are also additional sharp structures, especially for bcc, where $I(0)$ is reduced substantially below the so-called "lower limit" mentioned above. These are due to strong asymmetries of occupation in (3.10) and large values of $\partial n_i(E)/\partial E$ at $E=E_F$ found at the edges of the subbands of $\varepsilon_\nu(\mathbf{k})$. The addition of correlation modifies these structures slowly and adds a few new broader features (Fig. 1). Part of the correlation corrections will be discussed below. Thus Fig. 1 indicates that $I(0)$ should indeed depend on structure and species. Of course, varying the degree of band filling is not a very physical operation, but to some degree it can represent the effect of alloying, and also the variations seen would be comparable to those in changing from one crystal structure to another. Incidentally it should be noted that all our calculations are performed with the rigid-band approximation in (2.7). Additional degrees of freedom related to changes in the partial densities of states might modify some of the trends noted above. Similarly, we have not allowed any net redistribution of charge between the e_g and t_{2g} orbitals due to correlations.

It is interesting to consider next the variation of the ratio J/U, particularly for different band fillings. We take our model for Fe with $n=7.4$ electrons and $M_0=2.2$ magnetons. The bandwidth is fixed. This implies from (3.10) that $I(M_0)$ is fixed (0.624 eV). Some pairs of values (U,J) were determined which are consistent with the fixed W, M_0 and $I(M_0)$. Since $I(M_0)$ is fixed, it is useful to look again at the other limit $I(0)$. The results are shown in Table I. As can be seen, $I_{\mathrm{SCF}}(0)$ is roughly equal to $I_0(1.5)$ indicating as expected from (3.6) that exchange interaction between all pairs of orbitals plays a role. The small deviations of $I_{\mathrm{SCF}}(0)$ from I_0 and especially its scaling with $U+7J$ are due to the ΔJ and due to band structure effects as discussed in connection with (3.5) to (3.10). The most significant part of Table I is that $I(0)$ is roughly proportional to $U+6J$, which implies that even in the correlated state all five e_g and t_{2g} states and their interactions are roughly equally available for exchange. We note again the reduction of $I(0)$ from the value I_0 (1.5) for the reasons already discussed in connection with Fig. 1. We also note from Table I the variation of $I(M)$ as shown by the extreme values $I(0)$ and $I(M_0)$.

Tables II and III show similar results for fcc Ni ($N=9.4$, $M_0=0.6$) and fcc Co ($N=8.4$, $M_0=1.6$). They are both "strong" cases in the sense of Sec. II and we have fixed $I(M_0)$ (0.911 eV for Ni, 0.939 eV for Co) at slightly above the value needed to fill the majority band completely. In each case $I_{\mathrm{SCF}}(0)$ is again nearly equal to I_0 (1.5). But now for Ni we have that $I(0)$ is proportional to $U+2J$. Roughly speaking, this arises because there is little chance of having more than one hole on any Ni atom at one time so that the hole effectively correlates with its own subband, leaving just the interaction $U+2J$. However, the story is more complicated in detail as is shown by the different scaling of I_2 (defined below), which does not include spin correlation effects given in Table II: Exchange interactions between different orbitals are relevant, but even in the nonmagnetic state of Ni, the spin correlations in (2.4) are already nearly perfect so that spin alignment by magnetization cannot do any better. The mechanism driving the magnetism in this limit of few holes is therefore the direct Coulomb interaction in (2.3). Incidentally a similar argument makes it surprising that $I_{\mathrm{SCF}}(0)$ for Ni (Table II) scales with $(U+6J)$, i.e., with (3.6a) with $m=5$. The density of states at the Fermi energy consists mostly of t_{2g} states so that we might expect $m_{\mathrm{eff}}=3$ in (3.6a) or $s=-\frac{1}{3}$ in (3.9) which gives $I_{\mathrm{SCF}}(0)$ scaling with $U+4J$. Corrections come from e_g contributions and from the other terms (3.10). In Co (Table III) $I_{\mathrm{SCF}}(0)$ again follows $U+6J$,

TABLE II. The same as in Table I for fcc Ni ($N=9.4$), showing also the proportionality of $I(0)$ to $(U+2J)$.

J/U	U/W	$5I_{\mathrm{SCF}}(0)/(U+6J)$	$5I(0)/(U+2J)$	$I(0)/I(M_0)$	$I_2(0)/I(0)$
0.1	0.887	1.010	0.831	0.845	1.067
0.15	0.813	0.994	0.832	0.840	1.101
0.2	0.750	0.982	0.834	0.837	1.133
0.25	0.697	0.974	0.837	0.836	1.164
0.3	0.651	0.967	0.840	0.836	1.194
0.4	0.575	0.957	0.848	0.839	1.247

TABLE III. The same as in Table I, but for fcc Co ($N=8.4$). The Stoner parameter $I(0)$ is found to be approximately proportional to ($U+3J$).

J/U	U/W	$5I_{\mathrm{SCF}}(0)(U+6J)$	$5I(0)/(U+3J)$	$I(0)/I(M_0)$	$I_2(0)/I(0)$
0.1	0.817	0.931	0.741	0.812	1.122
0.15	0.716	0.928	0.746	0.798	1.174
0.2	0.640	0.925	0.749	0.791	1.221
0.25	0.579	0.925	0.752	0.786	1.262
0.3	0.530	0.925	0.754	0.783	1.298
0.4	0.456	0.921	0.756	0.782	1.358

whereas $I(0)$ is proportional to $U+3J$. We interpret the latter result in a similar way to that for Ni: The interorbital term $(m-1)J$ in (3.6a) is strongly reduced (in fact reduced from $4J$ to about J) by correlations, relative to the intraorbital term $U+2J$ in (3.6a). Incidentally there is no significance to be attached to the absolute values of $I(0)$ for the specific metals in Tables I–III because they are determined by the parameters of the model, which in turn are fixed by the observed momenta and the bandwidth determined by conventional band structure calculations with the LDA.

Another conclusion from these calculations is that although the ratio U/J has been widely changed, only very small variations in J and in $I(0)$ arise. The large variation of U apparently does not influence the magnetic properties much. We will therefore in the following always stick to a ratio $J/U=0.2$.

As mentioned before, the values of U and J, as we have obtained them, compare well with the values obtained from gas phase multiplet splittings. As discussed in Appendix A, a perfect agreement may be reached for Ni and Co, while for Fe, the interaction parameters used here are 10% smaller than those obtained from experiments. We performed the calculations with a smaller ratio J/U than found in experiments. This guarantees that the interaction effects as they will be discussed in the following are underestimated rather than overestimated.

As a conclusion, we obtain a strong variation of I with band filling and a sensitive dependence on details of the interaction. All these dependencies are well understood.

IV. MAGNETIZATION DEPENDENCE OF THE STONER PARAMETER

Of special interest is the variation of $I(M)$ with the degree of polarization M for fixed band fillings. Such a discussion will give some insight into how the correlation effects work in detail. The results are given in Figs. 2–4 for Fe, Co, and Ni, respectively, and compared with the function $D(M)$ which gives the differential loss of kinetic energy in Eq. (1.4). In Fe the M_0 is determined by the crossing of the two curves (Fig. 2), whereas Co and Ni are "strong" ferromagnets in the sense of Sec. I so that the majority band saturates before the condition (3.1) is reached. In all three cases $I(M)$ shows significant variation. In Fe (Fig. 2) this variation is rather complex. This is due to a changing mixture of e_g and t_{2g} orbitals in the moment as discussed in (3.6)–(3.9), responsible particularly for the drop in $I(M)$ beyond $M\approx 1.0$. We can verify this explanation by a small trick. The computations actually employ the partial density of states for each orbital rather than the wave function explicitly. Thus by averaging over the e_g and t_{2g} partial densities of state we can simulate a more isotropic system in which correlations can occur equally between all five orbitals, though the overall variation in the total density of states remains unchanged. Such a calculation results in the smooth curve $I'(M)$ in Fig. 2, of similar shape to $I(M)$ in Co and Ni.

In Co and Ni the situation is simpler. The $I(M)$ (Figs. 3 and 4) [and similarly $I'(M)$ for Fe (Fig. 2)] increase steadily with M, which can be understood in terms of spin-dependent correlations. As we have already remarked above, such correlations serve to depress $I(M)$ for small M but get progressively eliminated as M increases to saturation. This is demonstrated clearly by the calculations of $I_2(M)$ defined by excluding from the wave

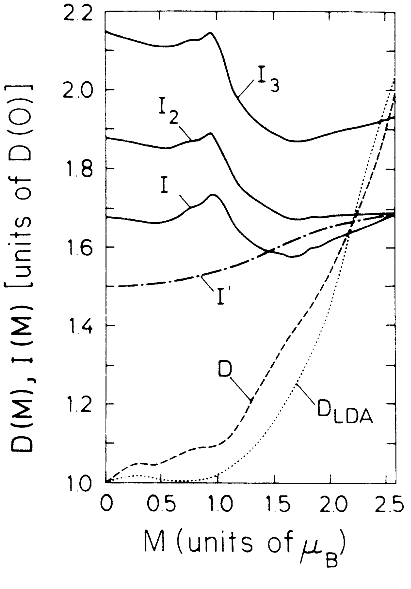

FIG. 2. Stoner parameter I and loss of kinetic energy $D(M)$ for different values of the ground state magnetization M for bcc Fe ($N=7.4$, $U/W=0.42$, $J/U=0.2$), normalized by $D(0)$. The curves I_2 and I_3 correspond to the calculations which neglect spin correlations (I_2) and neglect all correlation effects due to exchange interaction (I_3), respectively. I' is the Stoner parameter obtained from an average isotropic change distribution. D_{LDA} gives the loss of kinetic energy as obtained from the exact density of states within LDA for nonmagnetic Fe (Ref. 48), normalized in such a way that $D(M_0)=D_{\mathrm{LDA}}(M_0)$.

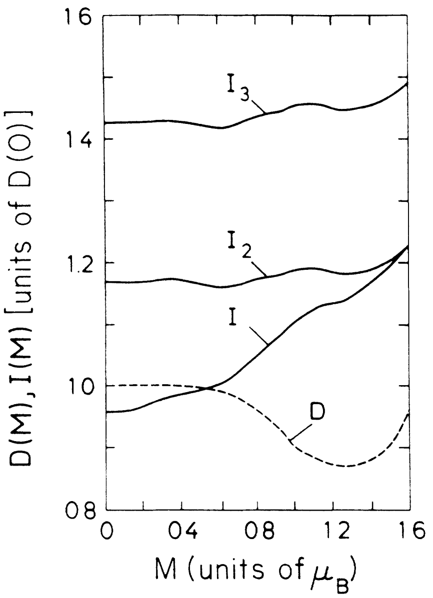

FIG. 3. Stoner parameter I and loss of kinetic energy $D(M)$ for different values of the ground state magnetization M for fcc Co ($N=8.4$, $U/W=0.64$, $J/U=0.2$), normalized by $D(0)$. The meaning of I_2 and I_3 as in Fig. 2.

function (2.4) all the spin-spin correlations in (2.6). Figures 2–4 show that $I_2(M)$ is larger than $I(M)$ and that the two become equal for a saturated majority band. This completely explains the 20% rise in $I(M)$ for Ni and Co while for Fe the effect of orbital anisotropy remains and is in fact more clearly seen in $I_2(M)$ without the masking effect of the spin correlations. We can calculate a fictitious isotropic $I_2'(M)$ analogous to $I'(M)$, which turns out to be practically a constant (not shown in Fig. 2) with $I_2'(0)-I'(0)$ being nearly equal to $I_2(0)-I(0)$, thus verifying our picture.

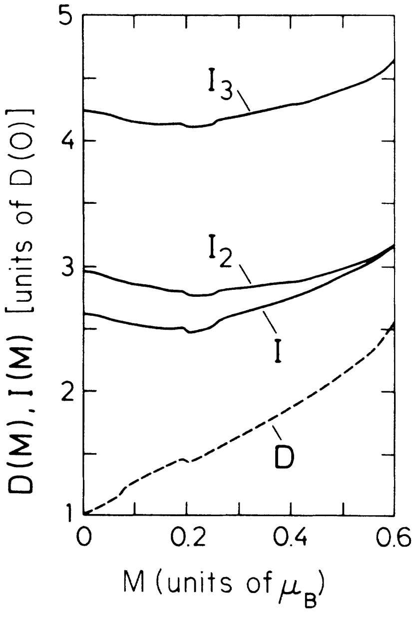

FIG. 4. Stoner parameter I and loss of kinetic energy $D(M)$ for different values of the ground state magnetization M for fcc Ni ($N=9.4$, $U/W=0.75$, $J/U=0.2$), normalized by $D(0)$. The meaning of I_2 and I_3 as in Fig. 2.

Having discussed so far how correlation effects enter the Stoner parameter, we must compare these results with those obtained within the LDA. The latter is the standard approximation scheme for the treatment of electronic properties in solids, including transition metals. As discussed in Secs. I and III, the Stoner parameter I obtained in LDA is rather a constant without much dependence on magnetizations or band filling.[4,6,11–14] However, our $I(M)$ depends noticeably on all of these, and we need to understand how such effects are left out of the LDA. The dependence of $I(0)$ on band filling arises even in a proper HF theory from the varying admixture of e_g and t_{2g} at E_F as shown in Eqs. (3.6)–(3.9) and carries over into the correlated calculations. While we have not properly optimized these anisotropy dependencies within our rigid-band treatment, the variation of I with M goes to the heart of the magnetic effects in LDA. Contrary to our findings that there is always a contribution to I which leads to a sizable increase with rising M, in LDA usually no M dependence[12,13] or even a small decrease with rising M was found.[14] In this context it is important to discuss the atomic limit first. As already mentioned in connection with Eq. (1.4), when calculating the ground state of atoms, LDA needs to be applied to a wave function with a broken spin symmetry. The ground state according to Hund's rule is then obtained. When not breaking spin symmetry, i.e., staying strictly within density functional theory and LDA, it has been found empirically that one obtains a state whose energy is the average over all possible magnetic configurations. The Hund's-rule spin ordering and its effect on the energy are therefore obtained only by an additional breaking of spin symmetry. This finding is not disturbing, because in atoms the symmetry is always broken. But when we switch to a molecule consisting of two atoms at very large distances we know that in this case the ground state is always a singlet state, with no broken symmetry. So a proper density functional should give the ground state energy of the Hund's-rule ordered atoms coupled weakly antiferromagnetically. However, LDA without broken symmetry gives an energy which is the sum of two atomic energies averaged again over all Hund's-rule states. Thus the LDA does not include any of the Hund's-rule corrections when they are to be included as spin correlations.

When atoms are connected to form a solid, then a computation in LDA will never obtain these spin correlations unless again the spin symmetry is broken. However, these correlations which are generalizations of Hund's-rule effects are present in a solid whether there is global magnetic order or not. LDA has to be considered, therefore, as a mean field theory with respect to Hund's rule or spin correlations. It can include those corrections only by breaking symmetry globally (in a magnetic ground state) or locally (for instance, in representations of the paramagnetic state with the coherent potential approximation).

To estimate the importance of the errors in the LDA, we can simulate the effect of neglecting Hund's-rule effects in our calculations. To some extent we have already done this in our calculations of I_2 in Figs. 2–4. It shows that neglect of spin-dependent correlations of type $O_{ij}^{(3)}$ enhances $I(0)$ artificially by 10%–20%, which we believe is a lower limit to the errors in LDA. We can set an upper limit on the effect by another calculation, I_3 in Figs. 2–4, obtained as follows. We assume that not only the spin correlations are omitted but that all terms in the Hamiltonian which are of the same nature as those leading to spin correlations are covered in LDA in one particle approximation only. These are all terms proportional to J and ΔJ in (2.3). Therefore, we first calculate a correlated ground state, omitting all these exchange terms from the Hamiltonian. One effect of this is to eliminate automatically any spin-dependent correlations in (2.6). We then reintroduce these terms of H_I (2.3) by adding to the energy their expectation value with respect to the uncorrelated wave function. This upper limit is by another 10%–20% higher than $I_2(M)$. By combining these lower and upper limits we can say that $I(0)$ is overestimated by 12%–22% for Fe, by 18%–33% for Co, and by 10%–40% for Ni. Table IV contains some LDA values for the Stoner parameter I and in addition the corrected values as obtained by such a renormalization. A direct comparison of our values of I with those of LDA computations is hampered because our model Hamiltonian is too limited, omitting as it does the *sp* hybridizations and relaxation effects correcting the rigid-band approximation.

The major point about this discussion is that for the theory of magnetism the relevant quantity is not $I(0)$ but rather the energy gain due to magnetization

$$E_0(M_0)-E_0(0)\approx\tfrac{1}{4}[D(0)-I(0)]M_0^2 = -\tfrac{1}{4}\xi D(0)M_0^2 \ , \quad (4.1)$$

with

$$\xi=I(0)/D(0)-1 \ . \quad (4.2)$$

This follows from rewriting (1.4) for small M_0. The relevance of (4.2) to the Stoner criterion (3.1) is obvious, but note that the energy of magnetization is also proportional to ξ. Clearly errors in $I(0)$ translate into much larger percentage errors in ξ, especially near the Stoner threshold for magnetization $\xi=0$. Table IV shows that ξ changes by up to a factor of 3 for the metals Fe, Co, and Ni.

TABLE IV. The LDA values of the Stoner parameter I and the relative energy gain per magnetization ξ as taken from Refs. 11 and 12, and compared with the correlated values of ξ (ξ_1 upper, ξ_2 lower limit).

	I_{LDA} (eV)	ξ_{LDA}	ξ_1	ξ_2
Fe	0.92	0.43	0.26	0.14
Co	0.99	0.6	0.31	0.08
Np	1.01	1.03	0.81	0.32

Our suggested corrections to LDA are therefore of vital importance to any thermodynamic theory, for example to estimate the transition temperature T_M. Consider the simplest case, the Stoner mean field theory.[1] When applied to Fe with the LDA value of I (Table IV) it gives a T_M (Stoner) of 4400 K,[12] but when correcting the I_{LDA} then a T_M (Stoner) is obtained in the range 3400–2300 K.[31] This is still much higher than the observed T_M of 1000 K, indicating that this transition can be understood only by including spin fluctuations. Using a magnetic energy reduced from LDA computations by a similar amount as the one found here, Mohn and Wohlfarth[44] managed to explain this magnetic transition in terms of such spin wave fluctuations with a theory which was based on the idea of Lonzarich.[45]

If there are such sizable corrections to $I(0)$ and even more to ξ, how does LDA give the equilibrium moments M_0 so well? Indeed this was one of the first important successes of LDA. However, for Fe, Co, and Ni some rather gross features of the energy bands suffice to explain the moments.[46,47] As is well known, the band energy $E_K(M)$ increases rapidly with M when $n(E)$ is low, and this stops further growth of M. Thus in the fcc metals Co and Ni the M_0 is determined by the filling of the majority spin band.[46] Since in bcc Fe, the majority d band is not completely filled, it seems worthwhile to cover this case in more detail. Here M_0 is determined by the dip in $n(E_F)$ in the middle of the band.[47] In Fig. 2 we see indeed the rapid rise of $D(M)$ around M_0, and this is not very different in our five-band model from the D_{LDA} calculated from a full LDA band structure.[48] The steepness of the curve ensures that M_0 does not depend too sensitively on the value of $I(M)$ one chooses (within reason).

The errors in $I(M)$ from spin correlations are less for M near saturation than for $M=0$, as we have seen. Nevertheless, the difference between using $I(M)$ and $I_2(M)$ or $I_3(M)$ amounts to a change of 4%–12% using our $D(M)$ or to a somewhat smaller change of 2%–8% using $D_{\mathrm{LDA}}(M)$. This explains the fact that the LDA moments calculated at the measured lattice constant are 2%–5% too high.[38]

V. VOLUME DEPENDENCE OF THE STONER PARAMETER

We next discuss the dependence of I on volume V. The volume enters the model Hamiltonian only indirectly through the bandwidth W which is a strong function of V, and possibly some volume dependence of U. It has been discussed above that the Stoner parameter $I(0)$ depends strongly on U/W. The numerical results obtained for Fe, Co, and Ni are displayed in Figs. 5(a)–5(c). The figures show that $I(0)$ at first decreases rapidly with $U/W\leq 0.1$ as can be verified by perturbation theory. For larger values of U/W, the decrease of $I(0)$ with increasing U/W is weaker due to higher order terms which mostly describe the mutual screening of the correlated d electrons among themselves.

Note that the effects shown in Figs. 5(a)–5(c) are on the whole larger than the other variations of $I(0)$ which we have discussed so far. Moreover, the monotonic de-

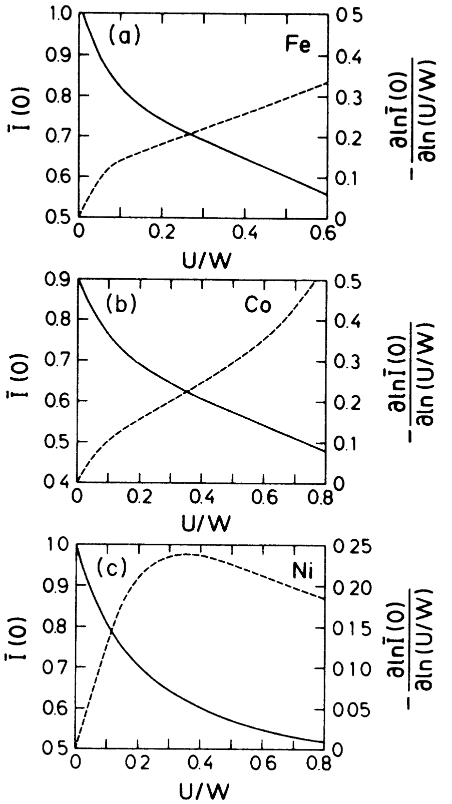

FIG. 5. $I(0)$ as depending on the ratio U/W for Fe (a), Co (b), and Ni (c). In addition the logarithmic derivations $-[\partial \ln\bar{I}/\partial \ln(U/W)]$ are given (dotted line).

TABLE V. Stoner parameter and its kinetic energy contributions for Fe, Co, Ni in units of the respective bandwidth W.

	$D(0)$	$I(0)$	$D'(0)$	$I_I(0)$	$I_{\mathrm{HF}}(0)$
Fe	0.070	0.118	−0.036	0.082	0.194
Co	0.159	0.154	−0.061	0.093	0.265
Ni	0.069	0.175	−0.034	0.141	0.329

crease of $I(0)$ with U/W has a ready physical explanation. It costs kinetic (band) energy to produce spatial correlations. Thus the larger V, the smaller W, and the more easily the electrons can correlate. Such correlation describes a mutual screening of the interaction of the electrons and therefore reduces I. However, the detailed behavior of the kinetic energy is quite complicated. In order to quantify it, we define below the part of kinetic energy which is lost due to electron correlation. The total kinetic (band) energy may be written as follows:

$$E_{\mathrm{kin}} \equiv \langle H_0 \rangle = E^0_{\mathrm{kin}} + E'_{\mathrm{kin}} \; , \tag{5.1}$$

where E^0_{kin} is the one-electron band energy for $U=J=0$, and E'_{kin} is the change of band energy due to correlation. The derivative of the first part, E^0_{kin} with magnetization, was expressed by the second term in Eq. (1.4), as $D(0)$. The derivative of the loss of kinetic energy due to correlation, E'_{kin}, is given accordingly in a similar way by

$$D'(0) = \lim_{M\to 0} 4[E'_{\mathrm{kin}}(M) - E'_{\mathrm{kin}}(0)]/M^2 \; . \tag{5.2}$$

Analogously, the change of the interaction energy due to electron correlations has the form

$$I_I(0) = -\lim_{M\to 0} 4(\langle H_I \rangle_M - \langle H_I \rangle_0)/M^2 \; . \tag{5.3}$$

Both $D'(0)$ and $I_I(0)$ contribute to $I(0)$. Numerical results are presented in Table V. As can be seen when comparing $I_I(0)$ and $I_{\mathrm{SCF}}(0)$, correlations screen more than 50% of the interaction contributions to $I_I(0)$. The corrections due to the decrease of kinetic energy which enter $I(0)$ compensate less than 30% of these losses in the final value of $I(0)$. As can be seen further when comparing $D(0)$ and $D'(0)$, correlation corrections of the kinetic energy terms are in between 40% (Co) and 50% (Fe,Ni). The fact that $D'(0)$ is negative is at first surprising. The loss of kinetic energy $E'_{\mathrm{kin}}(M)$ is of course positive, but it turns out to decrease with M. It is just a consequence of the fact that correlation effects are largest in the nonmagnetic state.

A convenient measure of these effects is the dimensionless ratio

$$r(U/W) = -\frac{\partial \ln\bar{I}}{\partial \ln(U/W)} \; , \tag{5.4}$$

shown in Figs. 5(a)–5(c) for Fe, Co, and Ni. It can be related to $D'(0)$ as we might expect from our preceding discussion (for details see Appendix B). We note [Figs. 5(a)–5(c)] that r rises steeply with U/W and then reaches a plateau of $r \approx 0.2$.

The experimental data obtained from magnetization experiments for nonmagnetic Ni and Pd alloys are usually analyzed in terms of the dimensionless derivative

$$f = \frac{\partial \ln I(0) D(0)}{\partial \ln V} \; , \tag{5.5}$$

as discussed in more detail elsewhere.[32] This quantity is related to r via

$$f = g(1-r) \; , \tag{5.6}$$

where we introduced for convenience

$$g = \frac{\partial \ln D(0)}{\partial \ln V} \; . \tag{5.7}$$

The quantity g covers the volume dependence that comes from the uncorrelated kinetic energy. The value r, therefore, is a measure of the correlation corrections.

While g is found to be between 1 and 2 (Ref. 4 and 49), the measured values of f lie between 0.6 and 1.[32] This suggests that the value of r should be positive and close to 0.5, in agreement with the results of the present calculations (see Fig. 5). Thus, the available experimental data support our result of a sizable volume dependence of I.

As discussed above, the principal origin of the volume dependence of the Stoner parameter is the loss of kinetic energy due to spatial correlations of electrons. This effect is missing in LDA, where the small dependence of the Stoner parameter on V enters only due to the volume dependence of exchange terms, but not for correlation contributions. This is the only dependence if one assumes, as in LDA, that the d electrons correlate like the homogeneous electron gas with a high density. As stated in the Introduction, fluctuations are completely screened over distances shorter than the atomic separations,[12] because strong correlations in the homogeneous electron gas over distances corresponding to the atomic separations would cost too much kinetic energy there, contrary to the real situation within the extreme tight-binding limit. Therefore, the resulting relative corrections of the volume dependence of the uncorrelated kinetic energy found in LDA are typically less than 5%.[50]

VI. PRESSURE AND MAGNETOVOLUME EFFECTS IN TRANSITION METALS

So far we have discussed correlation effects causing a volume dependence of the Stoner parameter I (Sec. V). In this section we will consider the consequences for the magnetovolume effect,[51] and more generally the analogous corrections for nonmagnetic transition metals to the equilibrium volumes calculated with the LDA. By magnetovolume effect we mean here the increase in equilibrium atomic (Wigner-Seitz) radius R due to the magnetization, compared with a hypothetical nonmagnetic state, all at $T=0$ K. Whereas in Sec. V we considered the differential quantity $I(M)$, the magnetovolume effect involves the integral over M^2 in the sense of Eq. (1.4).

The pressure can be formulated in terms of the electronic structure in various ways,[52-54] the most useful expression being (in our model) its relation to $E_{\text{kin}}(M)$ [Eq. (B4)]. Here it is assumed that U is independent of V. Note that Eq. (B4) applies with or without correlation, with or without magnetization. It can be interpreted as saying that the pressure of the electrons at the boundary of the Wigner-Seitz sphere is ultimately kinetic pressure due to band energy, no matter how this band energy arises. The derivative $(\partial W/\partial V)$ in Eq. (B4) can be evaluated by noting that $W \sim R^{-n}$ where $n=5$ for canonical bands and is about 4.5 in more detailed band structure calculations.[53] We can convert changes in P into changes ΔR in equilibrium values of R using the bulk modulus, which is roughly proportional to W. Altogether, we can write, therefore, an approximate relation

$$\Delta R \approx \alpha(\Delta E_{\text{kin}}/W) , \tag{6.1}$$

where we shall take below a constant value of α across the $3d$ transition series. ΔE_{min} stands here for the change of kinetic energy due to electron correlations.

Table VI shows the relevant parts of the kinetic energy as obtained from our calculations for the $3d$ transition metals. Note that E_{kin} is negative because it is measured from the center of the band, but an algebraic increase in E_{kin} corresponds correctly to an increase in pressure and hence R (6.1). The values of U/W are chosen arbitrarily for the nonmagnetic metals Sc-Ti to be 0.3 and for Cr and Mn to be 0.35. For Mn, an alternative computation was made in addition. It is known that in LDA one finds a stable ferromagnetic bcc state of Mn with $M=2.75$ magnetons.[55] The parameter U within our computation might be therefore obtained by looking for a ground state having the same magnetization. However, it turned out that it was impossible to get a stable magnetic moment of this size for Mn. Only when spin correlations were switched off could such a moment be stabilized for $U/W=0.6$, a surprisingly large value. Therefore we have done a second computation for Mn with this value. In LDA, the stable magnetic state is an antiferromagnetic state with $M=3.05$ magnetons.[55] Since we are not able to compute kinetic energies of such a state at present, we have determined the kinetic energies of the ferromagnetic state with the same moment instead.

As in Sec. V, the change of kinetic energy due to magnetization can be split as follows,

$$E_{\text{kin}}(M_0)-E_{\text{kin}}(0)=[E^0_{\text{kin}}(M_0)-E^0_{\text{kin}}(0)] +[E'_{\text{kin}}(M_0)-E'_{\text{kin}}(0)] , \tag{6.2}$$

where the first term is the one-electron energy and the second the additional band energy coming from correlation, corresponding to the terms in $D(M)$ and $I(M)$ in the total energy (1.4), respectively. Let us consider the results for Fe, being a typical example. One finds that the second term in Eq. (6.2) ($-0.029W$) is a 30% correction to the first one ($0.112W$) (see Table VI), giving a measure of how much the magnetovolume effect obtained in LDA is to be reduced.

Our main interest lies in corrections to equilibrium values of R. For this purpose, and incidentally to establish a convenient scale for α in (6.2), we must discuss again the LDA. The pressure from the d band in LDA is simply our E^0_{kin}. For the reasons already given (Sec. V),

TABLE VI. Kinetic energies of different states in units of the bandwidth W. Added are the structure, d band filling and ratio U/W used for the specific element.

Structure		N_d	U/W	$E^0_{\text{kin}}(0)$	$E^0_{\text{kin}}(M_0)$	$E_{\text{kin}}(0)$	$E_{\text{kin}}(M_0)$
Sc	fcc	2.4	0.3	−0.800		−0.755	
Ti	fcc	3.4	0.3	−0.969		−0.903	
V	bcc	4.4	0.3	−1.048		−0.973	
Cr	bcc	5.4	0.35	−0.992		−0.888	
Mn	bcc	6.4	0.35	−0.859	−0.569	−0.776	−0.524
	ferro		0.6			−0.495	−0.42
Fe	bcc	7.4	0.42	−0.692	−0.580	−0.617	−0.534
Co	fcc	8.4	0.64	−0.529	−0.437	−0.469	−0.386
Ni	fcc	9.4	0.75	−0.218	−0.207	−0.201	−0.191

the magnetic interaction $-IM_0^2/4$ is almost independent of volume in LDA and hence makes very little contribution to the magnetic pressure. Thus in a good approximation, the value of α may be determined from

$$[R(M_0)-R(0)]_{\mathrm{LDA}}=\alpha[E_{\mathrm{kin}}^0(M_0)-E_{\mathrm{kin}}^0(0)]/W \ , \tag{6.3}$$

where on the left we use the LDA values from Ref. 6 and the quantities from Table VI on the right. In this way, we find α to be in fact nearly the same for Fe, Co, and Ni, roughly equal to 0.5 a.u.

Let us consider first nonmagnetic 4*d* and 5*d* transition metals. Atomic correlations are present in these systems, similarly as in 3*d* materials. The respective correlation energy depends on the bandwidth which in turn depends strongly on the volume so that it generates an additional positive pressure, largely omitted in LDA. We believe that the *d* bonds in the 4*d* and 5*d* transition metals are sufficiently wide that this effect is unimportant. Indeed, the atomic radii calculated in LDA are in good agreement with experiment for these metals.[6] The main point is not that they are in such remarkably good agreement absolutely, but that the agreement is uniformly good from Zr to Ag (Refs. 6 and 40) and from Hf to Au.[40]

In contrast to this, the observed *R* for Sc to Ni are systematically larger than the nonmagnetic LDA values,[6] as shown in Fig. 6. This only partially improves when magnetic calculations are made. This is simply done for Fe to Ni.[6] For Mn, electronic pressures for different magnetic states at the experimental equilibrium distance have been published.[55] We used these to obtain or guess for the antiferromagnetic LDA equilibrium distance. The corrections due to correlations were then simply obtained by starting from $E_{\mathrm{kin}}(M)-E_{\mathrm{kin}}^0(M)$ for the magnetic and from $E_{\mathrm{kin}}(0)-E_{\mathrm{kin}}^0(0)$ for the nonmagnetic systems. For Mn, the ratio $U/W=0.6$ has been chosen. As can be seen from Fig. 6, the shift in lattice constants due to these corrections is roughly half the original difference.

In conclusion, we can summarize our results in Fig. 6 by saying that our correlation corrections have brought the calculated atomic radii into much better agreement with experiment, both for the nonmagnetic and the magnetic 3*d* metals. Our corrections in all cases do not go quite far enough but are in the right direction and of the right order of magnitude to reduce the discrepancy between calculated and measured atomic radius.

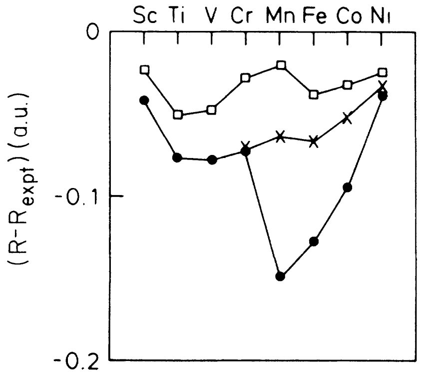

FIG. 6. Calculated values of the Wigner-Seitz atomic radii *R* relative to the observed ones, for the 3*d* transition metals. Dots—calculated by LDA for nonmagnetic state. Crosses—calculated by LDA for the magnetic state (Ref. 6). Squares—corrected from LDA values by our calculation.

ACKNOWLEDGMENTS

We want to thank Dr. A. B. Kaiser for many interesting discussions and Professor G. A. Sawatzky, Dr. O. Gunnarsson, and Dr. J. Zaanen for helpful comments. One of us acknowledges financial support of the Central Polish Research Project (CPBP) 01.09.

APPENDIX A: COULOMB AND EXCHANGE PARAMETERS FROM SPECTROSCOPIC DATA IN COMPARISON TO THE VALUES USED IN THIS WORK

Information about the Coulomb (U) and exchange (J) parameters for 3*d* transition metals may be obtained by analyzing the multiplet splittings of 3*d* elements, as discussed in detail by van der Marel and Sawatzky.[43] The experimental data suggest the use of semiempirical formulas[43]

$$U=1.5+0.21(Z-21) \ , \tag{A1}$$

$$J=\tfrac{5}{7}[0.59+0.075(Z-21)] \ , \tag{A2}$$

where the interaction parameters are given in eV. The factor $\frac{5}{7}$ in Eq. (A2) has been inserted in comparison to Ref. 43, because the exchange constant J as defined in Eqs. (2.1)–(2.3) differs from the one used there. This leads to $U=2.55$, 2.76, and 2.97 eV for Fe, Co, and Ni, respectively, and to a ratio $J/U=0.27$ independent of substance.

It is of interest to compare the above values of U and J for Fe, Co, and Ni, with the ones which we have obtained. When taking the bandwidth $W=5.43$, 4.84, and 4.35 eV for Fe, Co, and Ni, respectively,[40] then ratios U/W of 0.47, 0.57, and 0.68 are obtained. As can be seen from Tables I–III, these values together with the ratio J/U are reproduced for Co and Ni by a specific choice of our interaction parameters. For Fe, however, our interaction parameters are too small. When choosing the same ratio U/J, then U/W is 25% too small while, when choosing the same ratio U/W as obtained from Ref. 43, then J/U is 33% too small. Nevertheless, taking into account the qualitative nature of our model Hamiltonian and the completely different origin of both sets of data, there is surprising agreement, which strongly supports our choice of the model Hamiltonian. It should be noted that the direct experimental values[43] give an even better agreement with our parameters than the interpolated values. There, the ratios U/W were obtained as $U/W=0.43$, 0.55, and 0.74 for Fe, Co, and Ni.

Anyhow, the choice of parameters, made for our computations, represents in each case a lower bound for the parameters U/W and J/W for the transition metals Fe, Co, and Ni as compared with the gas phase spectroscopic data. Interaction effects, as they are discussed here, are therefore underestimated rather than overestimated.

APPENDIX B: RELATIONS BETWEEN $r(U/W)$ AND $D'(0)$

An alternative expression for $r(U/W)$ as defined in (5.4) can be derived, so that it is given explicitly as a function of $D'(0)$. In order to calculate $r(U/W)$ we first split $E_0(M)$ (1.4) into kinetic and interaction energy (for fixed N and M)

$$E_0(M)=Wf_{\rm kin}(\eta)+Uf_I(\eta)\ , \tag{B1}$$

respectively, where η stands for the set of variational parameters η_i in the wave function (2.4) which depends on U/W. Since the energy is a variational minimum we have

$$\frac{\partial E_0(M)}{\partial \eta_i}=W\frac{\partial f_{\rm kin}}{\partial \eta_i}+U\frac{\partial f_I}{\partial \eta_l}=0\ . \tag{B2}$$

The derivative of $E_0(M)$ with respect to volume V is

$$\frac{\partial E_0(M)}{\partial V}=\sum_i \frac{\partial E_0(M)}{\partial \eta_i}\frac{\partial \eta_i}{\partial V}+f_{\rm kin}(\eta)\frac{\partial W}{\partial V}+f_I(\eta)\frac{\partial U}{\partial V}\ . \tag{B3}$$

We use Eq. (B2) to eliminate the first term, Eq. (B1) to reexpress the second one, and drop the last term of Eq. (B3) by assuming that U is independent of V. As a result, we find an equation for the pressure of magnetic state,

$$P(M)=\frac{\partial E_0(M)}{\partial V}=\frac{E_{\rm kin}}{W}\frac{\partial W}{\partial V}$$
$$=\left[\frac{E^0_{\rm kin}(M)}{W}+\frac{E'_{\rm kin}(M)}{W}\right]\frac{\partial W}{\partial V}\ . \tag{B4}$$

Equation (B4) may be considered to be an exact result, which holds for an exact wave function with a large number of parameters η_i.

By taking the derivative of $P(M)$ with respect to $M^2/4$ at $M=0$,

$$\left[\frac{\partial^2 E_0(M)}{\partial (M^2/4)\partial V}\right]_{M=0}=\frac{[D(0)+D'(0)]}{W}\frac{\partial W}{\partial V}\ , \tag{B5}$$

one finds that the result is determined by the quantities $D(0)$ and $D'(0)$ introduced above. Independently, the derivative (B5) can also be obtained from Eq. (1.4).

By comparing both expressions, one finds that

$$\frac{\partial I(0)}{\partial V}=-\frac{D'(0)}{W}\frac{\partial W}{\partial V}\ . \tag{B6}$$

Therefore the quantity r, as defined in Eq. (5.4), is rewritten in terms of the derivative of $E_{\rm kin}$ as follows:

$$r(U/W)=-D'(0)/I(0)\ . \tag{B7}$$

---

[*] Permanent address: Institute of Physics, Jagellonian University, PL-30059 Kraków, Poland.

[†] Permanent address: Cavendish Laboratory, Cambridge CB3 0HE, England.

[1] E. C. Stoner, Proc. R. Soc. London Ser. A **165**, 372 (1938).

[2] E. P. Wohlfarth, Proc. R. Soc. London Ser. A **195**, 434 (1949).

[3] U. K. Poulson, J. Kollar, and O. K. Andersen, J. Phys. F **6**, L241 (1976).

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

[5] J. Callaway, in *Physics of Transition Metals, 1980,* Conference Series No. 55, edited by P. Rhodes (Institute of Physics, Bristol, 1981).

[6] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[7] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964).

[8] W. Kohn and L. J. Sham, Phys. Rev. **140**, 1133 (1965).

[9] S. H. Vosko, J. P. Perdew, and A. H. MacDonald, Phys. Rev. Lett. **35**, 1725 (1975).

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

[11] J. Callaway and C. S. Wang, Phys. Rev. B **16**, 2095 (1977).

[12] O. Gunnarsson, J. Phys. F **6**, 587 (1976).

[13] J. F. Janak, Phys. Rev. B **16**, 255 (1977).

[14] P. M. Marcus and V. L. Moruzzi, Phys. Rev. B **38**, 6949 (1988).

[15] J. Kübler, Phys. Lett. **79A**, 210 (1980).

[16] M. V. You and V. Heine, J. Phys. F **12**, 177 (1982).

[17] A. J. Holden and M. V. You, J. Phys. F **12**, 195 (1982).

[18] L. M. Small and V. Heine, J. Phys. F **14**, 3041 (1984).

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

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

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

[22] M. C. Gutzwiller, Phys. Rev. Lett. **10**, 159 (1963).

[23] G. Stollhoff and K. B. Bohnen, Phys. Rev. B **37**, 4678 (1988).

[24] M. V. Ganduglia, G. Stollhoff, P. Fulde, and K. P. Bohnen, Phys. Rev. B **39**, 5156 (1989).

[25] E. P. Wohlfarth, Rev. Mod. Phys. **25**, 211 (1953).

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

[27] D. A. J. Bradbury and D. M. Edwards, Phys. Lett. **30A**, 301 (1969).

[28] J. Friedel and C. M. Sayers, J. Phys. (Paris) **38**, 697 (1977).

[29] F. Kajzar and J. Friedel, J. Phys. (Paris) **39**, 379 (1978).

[30] A. M. Oleś and G. Stollhoff, J. Magn. Magn. Mater. **54**, 1045 (1986).

[31] A. M. Oleś and G. Stollhoff, Europhys. Lett. **5**, 175 (1988).

[32] A. B. Kaiser, A. M. Oleś, and G. Stollhoff, Phys. Scr. **37**, 935 (1988).

[33] D. Penn, Phys. Rev. Lett. **42**, 921 (1979).

[34] A. Liebsch, Phys. Rev. Lett. **43**, 1431 (1979).

[35] G. Tréglia, F. Ducastelle, and D. Spanjaard, J. Phys. (Paris) **41**, 281 (1980).

[36] L. C. Davis and L. A. Feldkamp, Solid State Commun. **34**, 141 (1980).

[37] L. Kleinmann and K. Mednik, Phys. Rev. B **24**, 6880 (1981).

[38] For a detailed discussion, see, e.g., P. Fulde, Y. Kakehashi, and G. Stollhoff, in *Metallic Magnetism,* Vol. 42 of *Topics in Current Physics,* edited by H. Capellmann (Springer, Berlin-Heidelberg, 1987).

[39] O. K. Andersen and O. Jepsen, Physica **91B**, 313 (1977).

[40] O. K. Andersen, O. Jepsen, and G. Glötzel, *Highlights of Condensed-Matter Theory, LXXXIX Corso Soc. Italiana di Fisica* (Tipografia Compositori, Bologna, 1985), p. 59.

[41] G. Stollhoff and P. Fulde, Z. Phys. B **26**, 257 (1977); **29**, 231 (1978).

[42] G. Stollhoff and P. Fulde, J. Chem. Phys. **73**, 4548 (1980).

[43] D. v. d. Marel and G. A. Sawatzky, Phys. Rev. B **37**, 10674 (1988).

[44] P. Mohn and E. P. Wohlfarth, J. Phys. F **17**, 2421 (1987).

[45] G. G. Lonzarich and L. Taillefer, J. Phys. C **18**, 4399 (1985).

[46] J. C. Slater, Phys. Rev. **49**, 537 (1936).

[47] J. C. Slater and G. F. Koster, Phys. Rev. **94**, 1498 (1954).

[48] P. Mohn (unpublished).

[49] V. Heine, Phys. Rev. **153**, 637 (1967).

[50] O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen, and J. Kollar, Physica **86-88B**, 249 (1977).

[51] E. P. Wohlfarth, J. Phys. C **2**, 68 (1969).

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

[53] D. G. Pettifor, J. Phys. F **7**, 613 (1977).

[54] N. E. Christensen and V. Heine, Phys. Rev. **32**, 6145 (1985).

[55] J. Kübler, J. Magn. Magn. Mater. **20**, 107 (1980).