Electronic structure and magnetic properties of dilute Co alloys with transition-metal impurities

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We present *ab initio* nonrelativistic and relativistic calculations for fcc Co alloys with 3*d* and 4*d* elements. The calculations are based on the local-density approximation of density-functional theory and employ the Korringa-Kohn-Rostoker Green's-function method. Results are given for the density of states, the local moments and hyperfine fields of the impurities and their nearest neighbors. The calculated magnetic moments and hyperfine fields are in reasonable agreement with the experimental data.

I. INTRODUCTION

In the last few years considerable progress has been made concerning the local behavior of impurities in metals. The basic theoretical problem is the loss of translation symmetry of the crystal with the defect, so that band-structure methods cannot be applied. In the dilute limit, Green's-function methods[1,2] offer a convenient and elegant way to solve the inhomogeneous problem of a single impurity in an otherwise ideal crystal. These calculations are based on local-density-functional theory, and apply the Korringa-Kohn-Rostoker (KKR) Green's-function method for impurities. The calculations of magnetic moments and hyperfine fields in Fe and Ni alloys with 3*d* and 4*d* impurities[3–5] are in good agreement with experimental results.

The aim of this paper is to extend these calculations to Co alloys. This has been motivated partly by the fundamental and technological interest in Co alloys, partly also by the recent interest in magnetic layered systems like CoPd or CoCu. Here a proper understanding of the real interface structure and properties requires an intimate knowledge of the corresponding alloys.

We use the KKR–Green's-function method and the local-density approximation (LDA). The potential perturbation of the impurity and the first shell of neighbors are taken into account. We investigate the fcc phase of Co, which is the stable phase at $T>400$ K. Results of Jarlborg and Peter[6] show that all properties of Co not depending on the density of states at E_F are very similar for low-temperature (hcp) and fcc phases. For example, the magnetic moment in the fcc phase of Co is about $0.03\mu_B$ (2%) larger than in the corresponding hcp phase. We believe that the present calculations for the fcc phase are also relevant for the hcp Co alloys, which is supported by comparison with experimental data. For all impurities we perform nonrelativistic (NR) and scalar-relativistic (SR) calculations.

The outline of the paper is as follows. In Sec. II we describe the characteristic features of the present calculation method. In Sec. III we present results for the local densities of states (LDOS) of 3*d* and 4*d* impurities. In Sec. IV the calculated local moments of impurities and Co atoms on the first shell around the impurity are discussed. In particular the change of the magnetic moment of the impurity is investigated as a function of noninteger nuclear charges. Our results show that for Mn impurities in Co two solutions exist, a stable antiferromagnetic one and a metastable ferromagnetic one. In Sec. V we discuss the calculated results for the hyperfine fields of 3*d* and 4*d* impurities and of neighboring host atoms. We summarize the main results of the present paper in Sec. VI.

II. METHOD OF CALCULATION

We describe the calculational method only briefly, as it is the same as the one used by Blügel *et al.*[3] and described by Zeller.[4] Our calculations are based on multiple-scattering theory using the KKR Green's-function method.[1,2]

For a lattice of muffin-tin potentials centered at position $\mathbf{R}^n$, the Green's function can be expanded into eigensolutions of these spherically symmetric local potentials:

$$G(\mathbf{r}+\mathbf{R}^n,\mathbf{r}'+\mathbf{R}^{n'};E) = \sqrt{E}\,\delta_{nn'}\sum_L Y_L(\mathbf{r})H_L^n(r_>;E)R_l^n(r_<;E)Y_L(\mathbf{r}') + \sum_{L,L'} Y_L(\mathbf{r})R_l^n(r;E)G_{LL'}^{nn'}(E)R_{l'}^{n'}(r';E)Y_{L'}(\mathbf{r}') \,. \quad (1)$$

Here the vectors $\mathbf{r}$ and $\mathbf{r}'$ are restricted to the Wigner-Seitz cell, and $r_>$ ($r_<$) denotes the larger (smaller) value of $r=|\mathbf{r}|$ and $r'=|\mathbf{r}'|$. The subscript $L=(l,m)$ collectively denotes the angular momentum quantum numbers l and m, and $Y_L(\mathbf{r})$ are real spherical harmonics. The regular $R_l^n(r;E)$ and the irregular solutions $H_l^n(r;E)$ of the radial Schrödinger equation for the nth muffin-tin potential are defined by their asymptotic behavior outside the muffin-tin sphere of radius S:

$$R_l^n(r;E)=j_l(\sqrt{E}r)+\sqrt{E}\,t_l^n(E)h_l(\sqrt{E}r)\ ,$$
$$H_l^n(r;E)=h_l(\sqrt{E}r)\quad \text{for } r\geq S\ , \tag{2}$$

where j_l and h_l are the spherical Bessel and Hankel functions and $t_l^n(E)$ is the usual on-shell t matrix for the nth potential. All the information about the multiple scattering between muffin tins is contained in the structural Green's-function matrix $G_{LL'}^{nn'}(E)$. It can be related to its counterpart $\mathring{G}_{LL'}^{nn'}(E)$ for the host crystal by an algebraic Dyson equation

$$G_{LL'}^{nn'}(E)=\mathring{G}_{LL'}^{nn'}(E)+\sum_{n''L''}\mathring{G}_{LL''}^{nn''}(E)\Delta t_{L''}^{n''}(E)G_{L''L'}^{n''n'}(E)\ . \tag{3}$$

The summation goes over all sites n'' and angular momenta L'' for which the perturbation $\Delta t_{l''}^{n''}(E)=t_{l''}^{n''}(E)-\mathring{t}_{l''}^{n''}(E)$ between the t matrices of the crystal with and without defect is significant. In the calculations we take s, p, d, and f states (with angular momenta $l\leq 3$) into account. We allow the potentials of the first shell around the impurity to be perturbed. The potentials are assumed to be spherically symmetric inside the Wigner-Seitz sphere. Exchange and correlation effects are included through the local-spin density approximation of von Barth and Hedin, with the constants as given by Moruzzi, Janak, and Williams.[7]

In spin-polarized calculations one obtains different Green's functions G for majority (+) and minority (−) spins. Integration over all occupied states below the Fermi energy E_F leads to spin densities

$$n^{\pm}(\mathbf{r}+\mathbf{R}^n)=-\frac{1}{\pi}\int_{\infty}^{E_F}dE\ \mathrm{Im}G^{\pm}(\mathbf{r}+\mathbf{R}^n,\mathbf{r}+\mathbf{R}^n;E)\ . \tag{4}$$

The spin densities are calculated by the method of complex energy integration (Zeller, Deutz, and Dederichs[8]). After a self-consistent determination of charge densities and potentials, the final results for magnetic moments on impurity and neighbor sites are obtained to be

$$m=\int d\mathbf{r}[n^+(\mathbf{r})-n^-(\mathbf{r})]\ , \tag{5}$$

and local densities of states for both spin directions are given by

$$n^{\pm}(E)=-\frac{1}{\pi}\int d\mathbf{r}\ \mathrm{Im}\mathbf{G}^{\pm}(\mathbf{r},\mathbf{r},E)\ , \tag{6}$$

where the integrations are performed over Wigner-Seitz spheres around the impurity or the neighboring Co atoms.

We estimated relativistic corrections to the magnetic moments and to the hyperfine fields in the scalar relativistic (SR) approximation, in which the orbital contribution is neglected.

The most important contribution to the hyperfine field is the Fermi contact interaction.[9] In this approximation the hyperfine field is given by the spin density $m(0)$ at the nuclear position

$$H=\frac{8\pi}{3}\mu_B m(0)\ , \tag{7}$$

with

$$m(0)=\int^{E_F}dE[n^+(0,E)-n^-(0,E)]\ . \tag{8}$$

Here $n^{\pm}(0,E)$ are the local densities of states for spin-up and -down electrons at the nuclear position. In the relativistic case the spin density at the nuclear position has to be replaced by the average of the spin density over a region near the nucleus whose diameter is the Thomson radius (Blügel *et al.*[3]).

III. DENSITY OF STATES

The LDOS in the impurity Wigner-Seitz spheres for 3*d* impurities is shown in Fig. 1. The results for both spin directions are plotted with the energies given relative to the Fermi energy. The LDOS of a Co impurity in Co, i.e., the host density of states, is also shown as a reference.

For Ni and Cu impurities the minority LDOS is shifted to lower energies, and the *d* states are more or less filled. The majority LDOS for Ni and Co has practically the same shape and position. But the majority LDOS of Cu is shifted considerably to lower energies.

The minority LDOS of Fe shows a sharp virtual-bound-state (VBS)-like unoccupied peak above the Fermi level. This shift of the minority LDOS to higher energies compared to the LDOS in pure Co arises because for Fe the local Coulomb potential is less attractive. For Ni it is more attractive, with the corresponding shift of the minority LDOS to lower energies. On the other hand the exchange potential is larger (smaller) than for pure Co because the local moment of Fe (Ni) is larger (smaller) than the Co moment. For the majority states the larger (smaller) exchange potential and smaller (larger) Coulomb potential act in opposite directions, whereas for the minority states they act in the same direction. In total the majority states are almost unaffected and the majority band remains practically full, whereas the minority states are pushed to higher energies for decreasing atomic numbers.

The situation is similar to the behavior of Co and Fe impurities in Ni: In all these cases the majority band is filled and practically unperturbed, and the charge adjustment must be achieved by the minority band alone. Therefore the moment changes always in steps of 1 μ_B. Alloys of this sort are generally called strong ferromagnets, and their moments fall on the main branch of the Slater-Pauling curve.[10,11]

For Mn and earlier 3*d* impurities, the LDOS shows a very different behavior. In the majority band the weakening of the electrostatic potential with decreasing valence can no longer be counterbalanced by an increasing exchange potential, since the local moment cannot increase sufficiently. As a result, for Mn a virtual bound state moves out off the majority band to the Fermi energy, in this way slightly depopulating the majority band and thus destabilizing the ferromagnetic state. In fact, for Mn impurities both in Ni and Co two solutions exist: a ferromagnetic one ("Mn/*f*/") with a more or less completely filled occupied majority VBS, and an antiferromagnetic one ("Mn/*a*/") with a practically empty majority VBS.

The energy difference between both configurations was calculated by the total energy formalism developed by Drittler *et al.*[12] Three different exchange-correlation potentials were used, i.e., that of Moruzzi, Janak, and Williams[7] (MJW), Vosko, Wilk, and Nusair[13] (VWN), and von Barth and Hedin[14] (BH). Our calculations yield the antiferromagnetic state as the ground state, being 0.129 eV (MJW) [0.128 eV (VWN), 0.163 eV (BH)] lower in energy than the metastable ferromagnetic state. For the earlier 3*d* impurities (Cr, V, Ti) only the antiferromagnetic solution survives. Since the moments are much smaller, the VBS's of both spin directions are at a similar energy position, with the minority peak somewhat more occupied. With decreasing valence both peaks move to higher energies.

The behavior of the LDOS for 4*d* impurities shown in Fig. 2 is different from that for the 3*d* impurities. One effect is the usually lower energy position of the 4*d* levels compared with the corresponding 3*d* levels, but the main effect arises from the larger spatial extent of the 4*d* wave

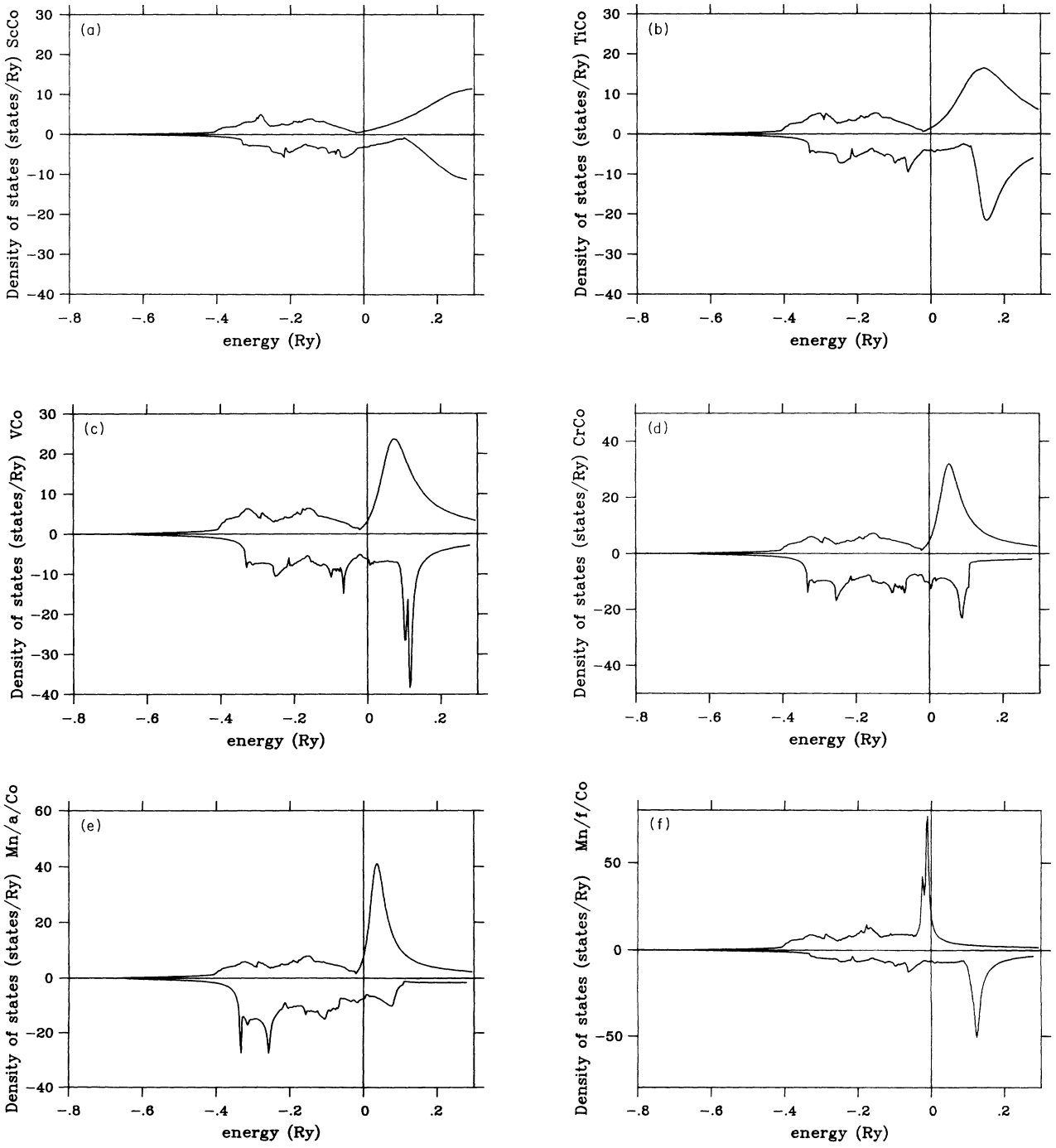

FIG. 1. Local densities of states of 3*d* impurities in Co for both spin directions.

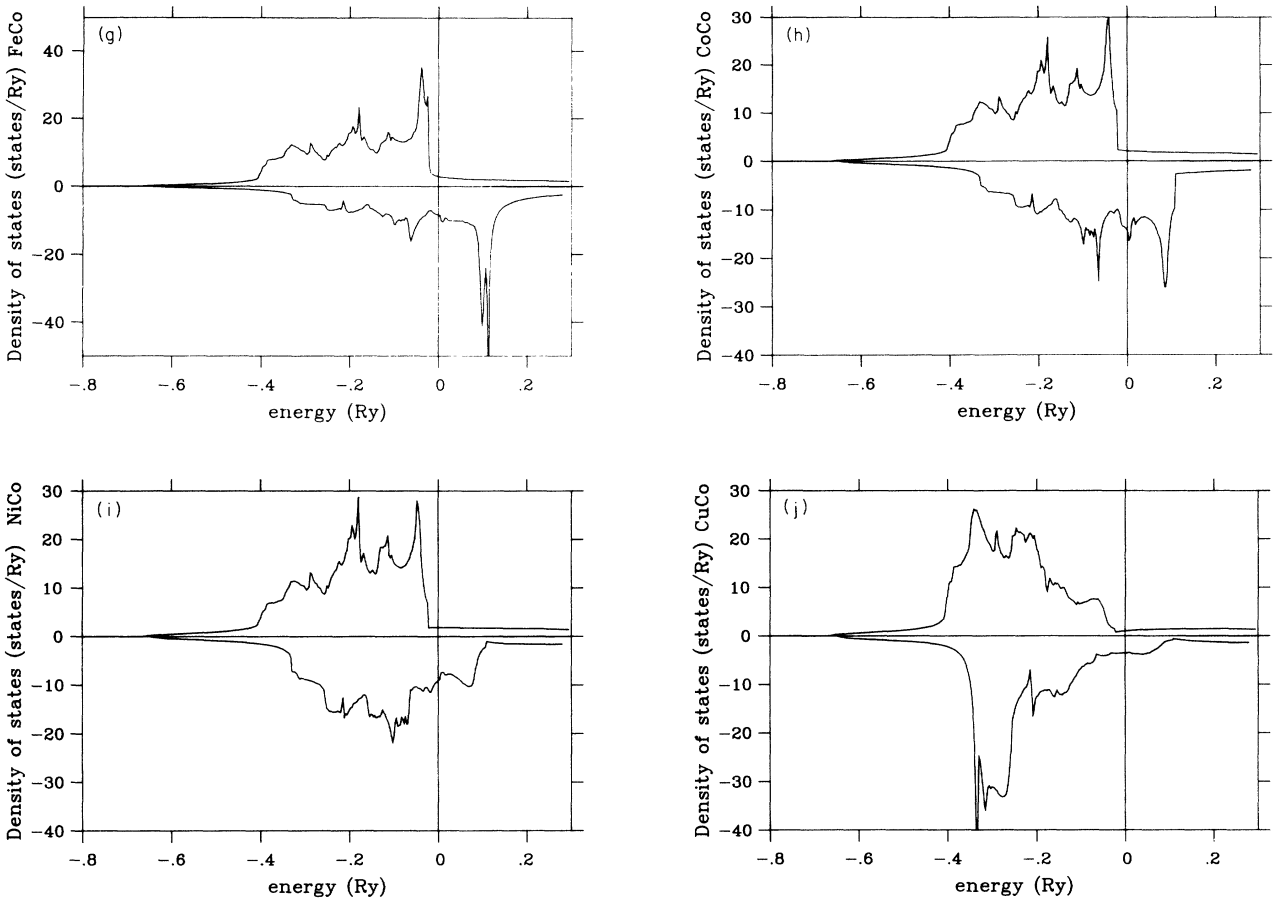

FIG. 1. (*Continued*).

functions. This leads to stronger hybridization with the Co valence states, and to broader impurity states. The broader bands and slightly smaller exchange integral make magnetism less favorable for 4*d* impurities. Thus both spin directions have rather similar LDOS with small exchange splittings. Due to the large 4*d* hybridization both bonding and antibonding hybrids are pushed out of the Co *d* band, leading to a two-peak structure in the LDOS, whereas their 3*d* counterparts have only one virtual bound state.

We can conclude that the main peculiarities of LDOS for transition-metal impurities in Co are similar to those in Ni.[4,5] Basically this arises from the fact that both hosts are strong ferromagnets with filled majority *d* bands.

IV. LOCAL MOMENTS

The calculated local moments of the 3*d* and 4*d* impurities in Co are shown in Figs. 3 and 4, together with the experimental data.[15–18] Unfortunately we are not aware of any experimental results for the magnetic moments of 4*d* impurities in Co. Here we present the results of SR calculations.

In general the agreement with the experimental data for 3*d* impurities is good. The somewhat controversial case of Mn impurities will be discussed below. For a detailed study of the behavior of the magnetic moment in the middle of the 3*d* series, self-consistent calculations for noninteger values of the atomic number Z have been performed (see Fig. 3). For the late 3*d* impurities only the ferromagnetic state survives, and for the early 3*d* impurities only the antiferromagnetic one, whereas in the middle of the series two states exist. This corresponds to the results for Ni.[4]

The major difference between the behavior of 3*d* impurities in Ni and Co, and of 3*d* impurities in Fe (Drittler *et al.*[5]) is the existence of a relatively large two-state region of magnetic state in Ni and Co, which is absent in Fe. In Fe the impurity moment for nuclear charges around $z=25$ (i.e., for Mn) changes sharply but continuously from positive to negative values, while the value for Mn itself is positive, but rather small ($0.69\mu_B$).[5] Contrary to that in Ni, a broad two-state region is found in the calculation,[4] extending nearly from $Z=24$ (Cr) to 26.5. In particular for Mn in Ni, both ferromagnetic and antiferromagnetic solutions with very similar moments of $2.9\mu_B$ are found, with the ferromagnetic solution being more stable by about 0.44 eV.[19] Comparing this with our results for the Co host, we see that in Co the two-state region is a factor 2 smaller, extending between $Z=24.7$ and 26. In this sense the behavior in Co is intermediate

between the broad two-state region in Ni and its disappearance in Fe. The basic reason for this difference is the increasing strength of the host polarization which destroys the near degeneracy of the two states, as has been discussed by Jo and Miwa.[20] Moreover our calculations show that for Mn in Co the antiferromagnetic configuration is more stable than the ferromagnetic one, though only by a rather small amount of 0.12 eV. The competition between both states might therefore be easily changed by a small perturbation, and along with the pseudoternary coherent potential approximation (CPA) calculations of Jo and Miwa[20] and Akai and Dederichs[21] for NiMn we expect both configurations as well as noncollinear orientations to occur for higher Mn concentrations.

Unfortunately the experimental information about Mn impurities in Co is controversial. From magnetization measurement, Crangle[22] obtains $\Delta M = -4.5\mu_B$ for the change of the total alloy moment per Mn atom, which would be in line with the antiferromagnetic

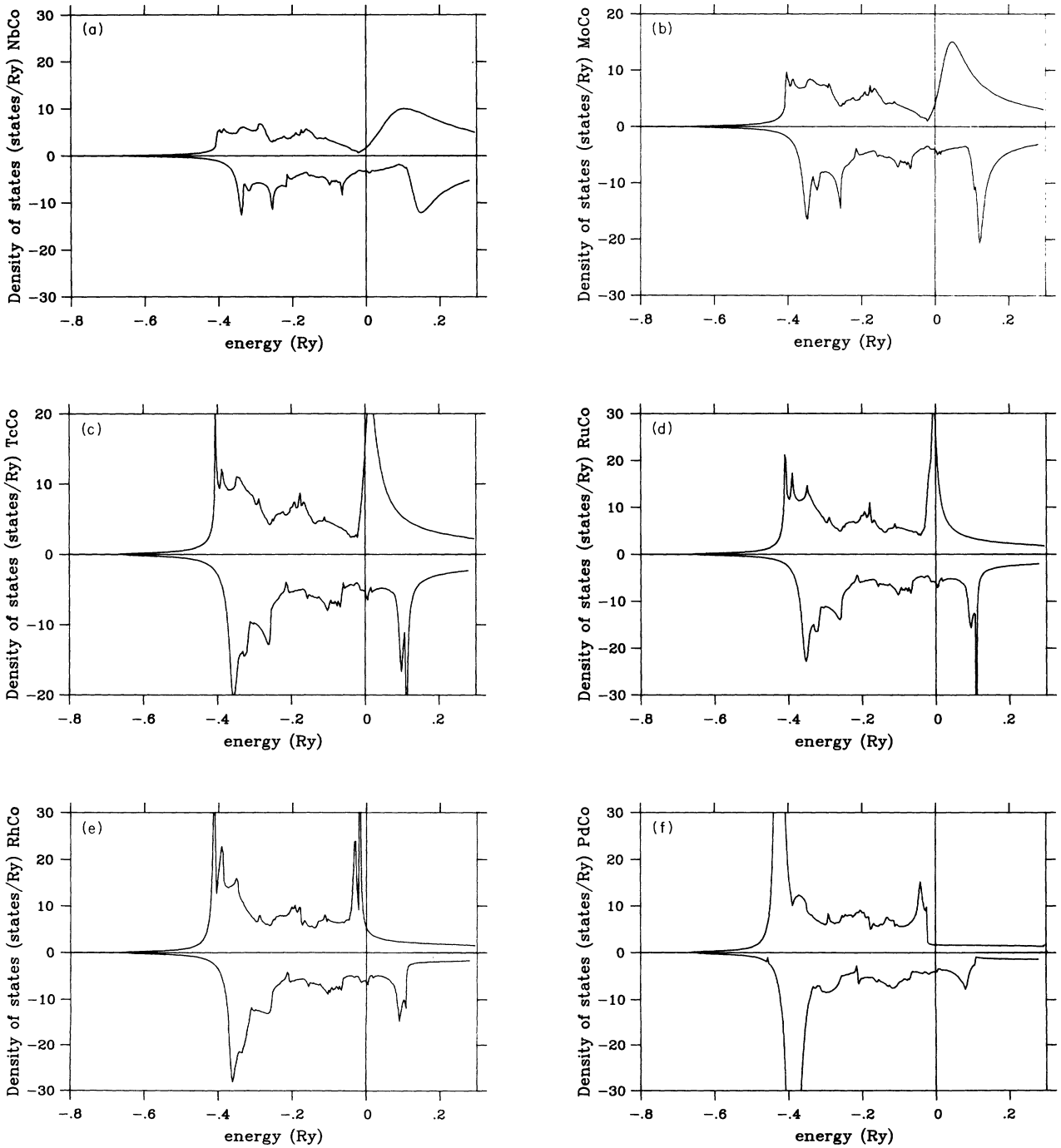

FIG. 2. Local densities of states of 4*d* impurities in Co for both spin directions.

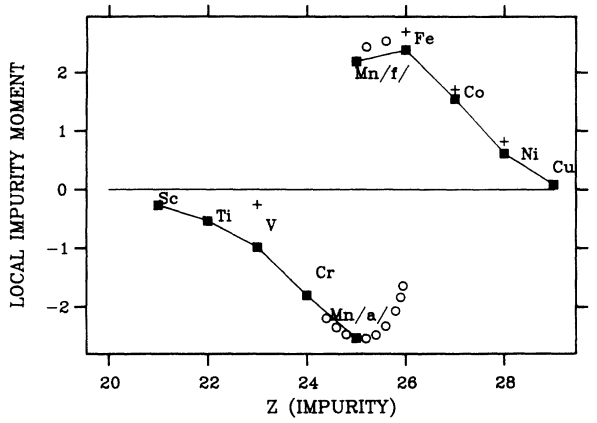

FIG. 3. Local moments in the impurity Wigner-Seitz sphere for 3*d* impurities in Co; squares: integer values of the atomic number; open circles: noninteger values of the atomic number; crosses: experimental values.

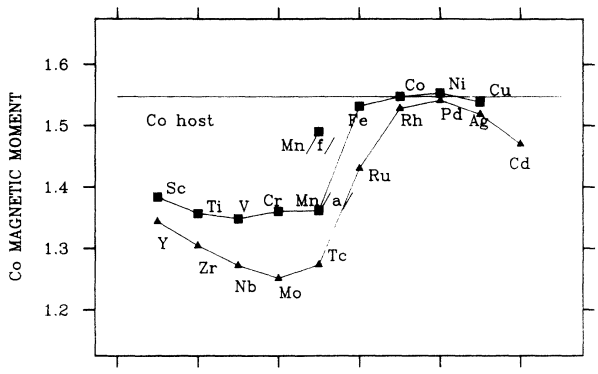

FIG. 5. Magnetic moment of Co atoms on the first shell around 3*d* and 4*d* impurities.

configuration. Neutron-scattering data by Nakai, Hozaki, and Kunitomi[23] point to the existence of two configurations, with the occupancy of the ferromagnetic one vanishing for small concentrations. Shiozaki, Nakai, and Kunitomi[24] study ternary $Ni_{1-x}Co_x$ alloys with 2% Mn impurities, and conclude that the Mn moment changes sign at a Co concentration of 50%, so that it is negative for pure Co. Cable and Hicks[25] and Cable[26] find small and antiferromagnetically aligned Mn moments of $-0.3\mu_B$ in relatively concentrated CoMn. Cable interprets this small value as the result of dynamical fluctuations between ferromagnetic and antiferromagnetic configurations with large positive and negative moments. In agreement with our calculations the experiments point to the existence of the antiferromagnetic configuration in the dilute limit; however, no direct information about the magnitude of the moment exists.

The changes of the magnetic moment on neighboring host atoms are shown in Fig. 5. The moment is only slightly changed when the impurity moment aligns to the host moments, but strongly decreases for the antiparallel configuration. This means that for the early transition-metal impurities the magnetic perturbation is rather extended. The strong reduction of the Co moment in the middle of the *d* series is directly related to the crossing of the majority VBS through the Fermi energy, and the transition from strong to weak ferromagnetism.

V. HYPERFINE FIELDS

Figures 6 and 7 show the calculated hyperfine fields (HF's) for 3*d* and 4*d* impurities in Co, and a comparison with the experimental data. For 4*d* impurities we present the NR as well as SR results. For 3*d* impurities we performed SR calculations as well. But the relativistic corrections are small (< 10%).

For 4*d* impurities the calculated values of the HF agree well with experiments.[27,28] In view of the results for neighboring elements Tc, Mo, and Nb, we believe that for Zr impurities the experiment had problems, and we consider the calculated data to be more reliable. From Fig. 7 one can see that SR corrections lead to considerable improvement of the NR values for Ru, Rh, Pd, and Ag. For 3*d* impurities we obtain good agreement for the hyperfine fields of Cu, Ni, V, and Sc impurities. Somewhat large deviations occur for Fe, which points to an underestimation of the core polarization in the local-

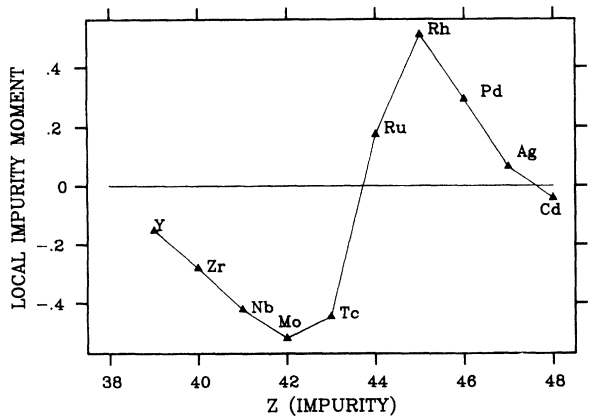

FIG. 4. Local moments in the impurity Wigner-Seitz sphere for 4*d* impurities in Co (SR results).

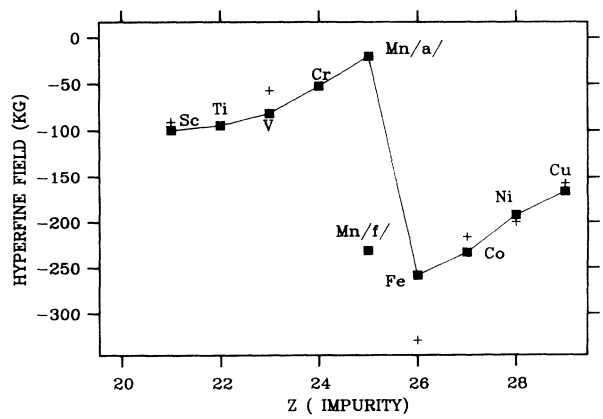

FIG. 6. Hyperfine fields for 3*d* impurities in Co; crosses: experimental values.

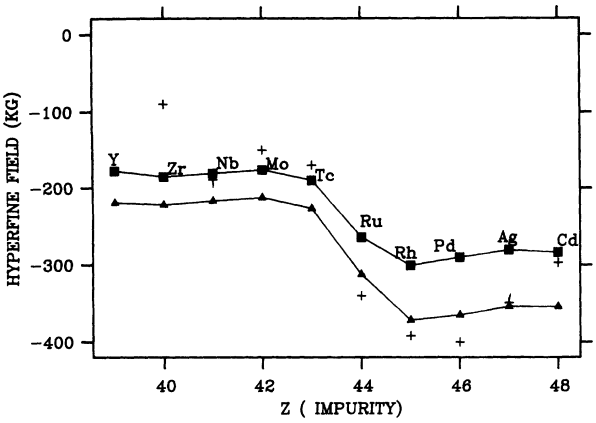

FIG. 7. Hyperfine fields for 4*d* impurities in Co; triangles: the SR results; crosses: experimental data.

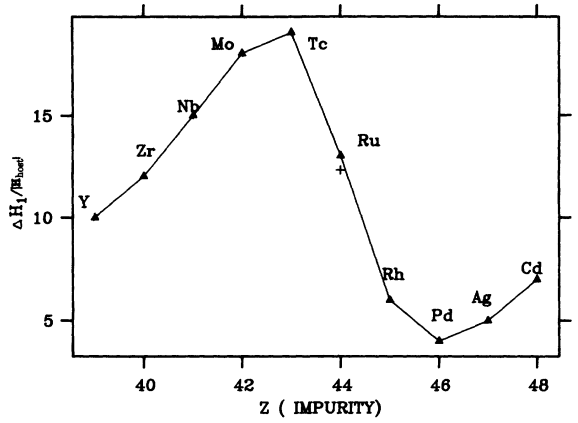

FIG. 9. Change of the hyperfine field of a nearest-neighbor atom for 4*d* impurities; triangles: the SR results.

density approximation, as discussed by Blügel *et al.*[3] A similar error is also expected for the ferromagnetic configuration of Mn. Experimentally a very large negative hyperfine field of −350–360 kG has been well identified by Yasuoka, Hoshinouchi, and Nakamura.[29] In ternary alloys of Co_{1-x} Ni_x with Mn impurities they find that the intensity of this line strongly decreases with increasing Co content, but the missing "main" line corresponding to the antiferromagnetic configuration is not found. There are, however, other reports from Cameron *et al.*[30], Kobayashi *et al.* (quoted in Kontani, Asayma, and Itoh[31]), and Campbell *et al.* (quoted in Rao[28]) about a positive hyperfine field of about +100 kG, which would fit well with our calculated hyperfine field for the antiferromagnetic Mn configuration, especially when one considers that a similar LDA error as for the ferromagnetic configuration must be expected, but with opposite sign. In total we believe that the available hyperfine data for Mn in Co, which at first sight look very contradictory, are basically in agreement with our results showing the preferred stability of the antiferromagnetic configuration. However, new experimental data about this controversial system are needed very much.

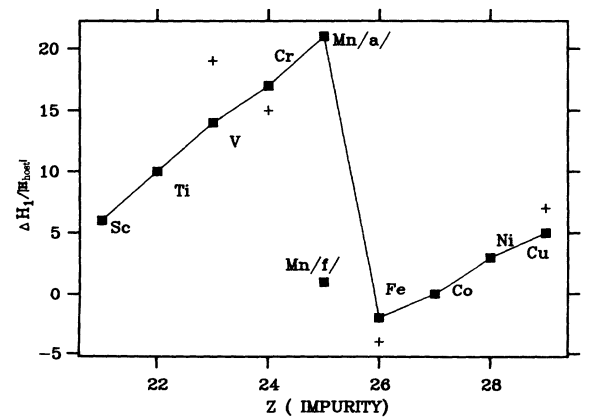

FIG. 8. Change of the hyperfine field of a nearest-neighbor atom for 3*d* impurities; crosses: experimental data.

Let us now consider the calculated changes ΔH_1 of the HF of first neighboring Co atoms. Figure 8 refers to 3*d* impurities, Fig. 9 to 4*d* ones. Given are the changes in percentage of the absolute value of the host HF H_{host}, i.e., $\Delta H_1/|H_{\text{host}}|10^2$. Positive (negative) values mean that the HF of the first neighbors is smaller (larger) than the unperturbed field of the host, which is negative. We can see that for 3*d* impurities the agreement with experimental data is very good. Unfortunately no experimental values for Mn exist, which according to our results would allow an independent determination of the local Mn moment. Due to the predicted large difference in the two configurations of the Mn impurity, Co NMR experiments for CoMn would be very desirable. For 4*d* impurities only one experimental result exists, i.e., for Ru. The agreement between theory and experiment[32] is good.

VI. SUMMARY

In this paper we have presented calculations for the LDOS, the magnetic moments, and the hyperfine fields for 3*d* and 4*d* impurities in Co. The calculations are based on density-functional theory in the local-density approximation, and apply the KKR–Green's-function method for impurity calculations. The impurity potential and perturbed potentials of the first shell of Co atoms are determined self-consistently. In general the results are in good agreement with experimental data.

For the Mn impurity we obtain two solutions with negative and positive moments. The calculated total energies show that the antiferromagnetic state is more stable than the ferromagnetic one. More experimental information about CoMn seems to be needed.

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