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Local spin moments of transition-metal impurities in monovalent simple-metal hosts

N. Papanikolaou and N. Stefanou
Solid State Section, University of Athens, Panepistimioupolis, New Buildings, GR-157 84, Athens, Greece

R. Zeller and P. H. Dederichs
Institut für Festkörperforschung, Forschungszentrum Jülich, Postfach 1913, D-5170 Jülich, Federal Republic of Germany
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The local magnetic properties of 3*d* and 4*d* substitutional impurities in noble and alkali-metal hosts are investigated by means of self-consistent local-spin-density-functional calculations using the jellium model as well as the first-principles Korringa-Kohn-Rostoker–Green's-function method. The results for the impurity moment from both calculations are in good agreement and compare well with the available experimental data. Our calculations give a consistent picture for the formation of local impurity spin moments in free-electron-like hosts.

I. INTRODUCTION

Since the work of Friedel,[1] the study of magnetic impurities in simple nonmagnetic metals has attracted considerable interest from the experimental as well as from the theoretical point of view.[2] The existence of a magnetic moment, more or less localized on an impurity, can be understood in the light of the Friedel's model,[1] which introduced the concept of the virtual bound state within the framework of scattering theory. The models of Anderson[3] and Wolff[4] rely heavily on Friedel's arguments. For single impurities the mean-field approximation of these models was successful in distinguishing the impurities into magnetic and nonmagnetic using the ratio of two parameters, the mean intra-atomic Stoner exchange energy I and the width Δ of the impurity virtual bound state. Other theoretical approaches have been undertaken within the framework of the ionic model.[5,6]

Blandin and Friedel[7] and Coqblin and Blandin[8] proposed a simple quantitative form[9,10] for the condition of the occurrence of a local spin moment $In_{\text{loc}}(E_F) > 1$. This condition is very similar to Stoner's criterion for band ferromagnetism. The only difference is that $n_{\text{loc}}(E_F)$ here denotes the paramagnetic local density of states of the impurity at the Fermi level. The condition of Blandin and co-workers simply expresses the fact that the nonmagnetic impurity state becomes unstable when the gain of the exchange energy is greater than the increase of the kinetic energy in the band when the two spin states are split.

The models mentioned above reveal the essential physical mechanisms which are responsible for the formation of a spin moment localized on the impurity. However, a reliable quantitative description of the electronic properties of a dilute alloy can only be achieved within the framework of a first-principles theoretical approach. Nowadays, new and more detailed information on the magnetic properties of impurities is coming from the self-consistent computational formalisms developed in recent years.

Calculations by the Korringa-Kohn-Rostoker–(KKR–) Green's-function method, which takes into account the full chemical environment of the impurity, have illuminated the problem of the magnetic behavior of 3*d* and 4*d* impurities in noble-metal hosts.[11–13] Cluster calculations have also been performed for magnetic impurities in Cu,[14–18] alkali metals,[19] alkaline-earth metals, and Al.[20] However, it is difficult to extract reliable information from these calculations if the size of the considered cluster is not large enough to ensure convergence. Recently, the jellium model was successfully applied to explain the formation of local moments of 3*d* impurities in noble- and alkali-metal hosts, by means of self-consistent electronic-structure calculations.[21]

In this work we seek to combine the explanatory power of the jellium model with the accurate description of the dilute-alloy system offered by the KKR–Green's-function method in order to investigate the local magnetic properties of 3*d* and 4*d* impurities in simple monovalent metal hosts. Contrary to what one might expect, transition-metal impurities in alkali-metal hosts are much more difficult cases than the same impurities in noble metals. First, there is a large size mismatch since transition-metal impurities are much smaller than the alkali-metal atoms. Thus one has to expect rather large lattice relaxations, which are not within the scope of the present paper. In certain cases even interstitial positions cannot be excluded. Second, it is experimentally well established[22–26] that most of the impurities carry, in addition to the spin moment, also a fully developed orbital moment. Unfortunately, the formation of orbital moments as required by Hund's second rule cannot be described by density-functional theory. Therefore the present calculations should be considered with caution when compared with the experimental data. The only result we can expect is to understand the trends for the formation of spin moments in the different simple-metal hosts.

II. CALCULATIONAL METHOD

The electronic structure of all the 3*d* and 4*d* substitutional impurities in monovalent hosts is calculated self-consistently by both the KKR–Green's-function method and the jellium model. The self-consistent one-electron potential of the dilute alloy is determined by an iterative procedure within the framework of density-functional theory.[27] The contribution of exchange and correlation effects is included through the local-spin-density approximation scheme of von Barth and Hedin[28] with the parametrization proposed by Moruzzi, Janak, and Williams.[29] Some of the calculations (see below) are also performed with the functional of Vosko, Wilk, and Nusair,[30] being based on exact Monte Carlo results for the homogeneous electron gas.

The KKR calculations are performed for the 3*d* and 4*d* impurities diluted in Cu, Ag, Li, Na, and K hosts. The details of the method can be found elsewhere.[11,12] The site-centered spherically symmetric potentials in a cluster consisting of the impurity and its 12 first neighbors in the case of fcc hosts (Cu,Ag) or the impurity and its 14 first and second neighbors for bcc hosts (Li, Na,K) are calculated self-consistently. The correct embedding of the perturbed cluster into the infinite host crystal is described by the Green's function of the host. Angular momenta up to $l_{\max}=3$ are included in the calculation.

In the jellium model, the Coulomb potential of the host-metal ions is replaced by a uniform positive background. This opens the possibility that the host-electron density can be varied continuously. The jellium model is therefore suitable to study the magnetic behavior of 3*d* impurities in free-electron-like metals. The details of the jellium calculational method can be found elsewhere.[21] For each of the 3*d* and 4*d* impurities, we varied continuously the jellium density $\bar{\rho}$ from a dilute limit corresponding to the Cs host up to the critical value $\bar{\rho}_c$, where the magnetic moment disappears. An angular momentum cutoff $l_{\max}=3$ and a range of the perturbing potential $S=10$ a.u. is usually sufficient to obtain good convergence in all cases examined.

III. RESULTS AND DISCUSSION

A. Local density states

In Figs. 1 and 2 we show the spin-polarized local densities of states of 3*d* impurities in Li and K as calculated by the KKR method. They are characterized by the presence of the impurity virtual bound state, which is about a factor of 5 narrower in the K than in Li host, because the hybridization of the atomic *d* state with the extremely dilute K-host free-electron gas is weaker than in the Li host. The position and width of the virtual bound states calculated by the KKR and the jellium methods are in very good agreement. Our KKR results for the 3*d* and 4*d* impurities in Cu and Ag agree with the results of previous KKR calculations.[11–13]

For the early transition-metal impurities, the minority-spin states are almost empty and the ionic charge of the impurity is screened by the majority-spin electrons. On the contrary, for the late 3*d* elements, the majority-spin states are almost completely filled and the screening is accomplished in the minority-spin subband.

In the case of 4*d* impurities, the densities of states ex-

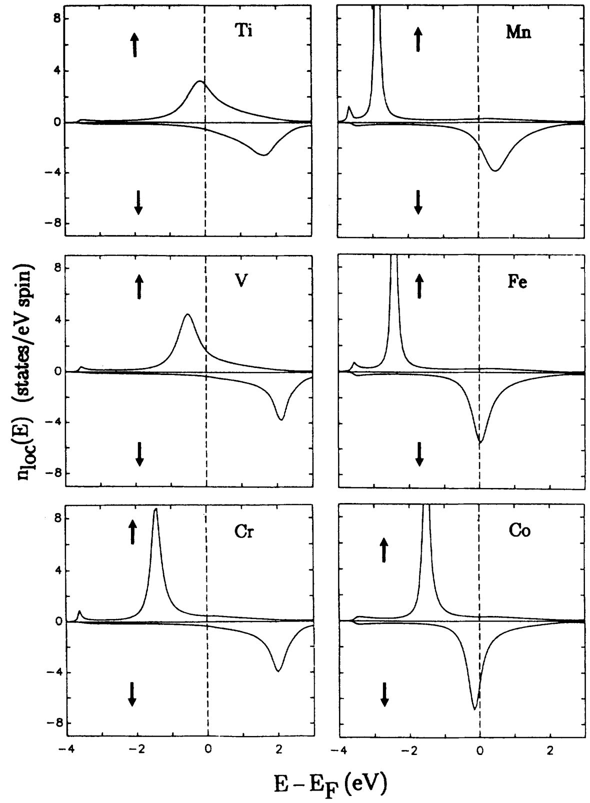

FIG. 1. Spin-polarized local density of states of 3*d* impurities in Li.

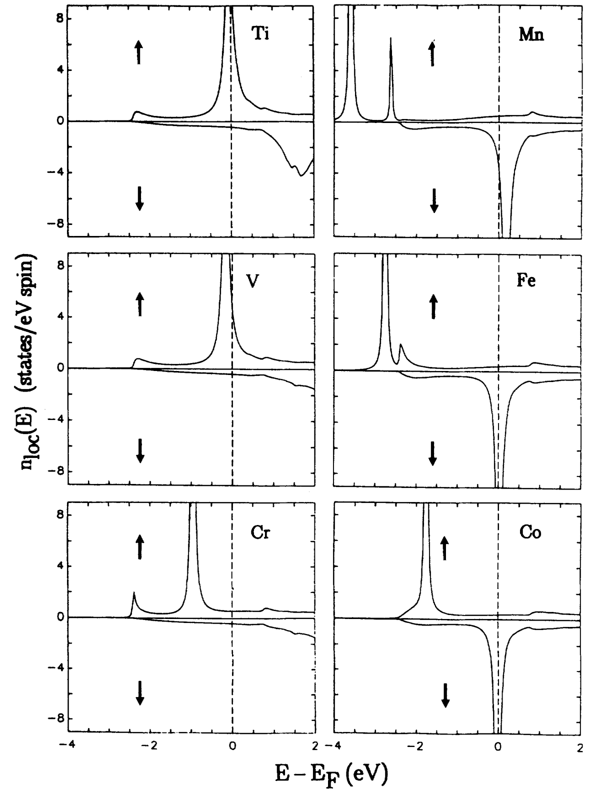

FIG. 2. Spin-polarized local density of states of 3*d* impurities in K.

TABLE I. Width Δ of virtual bound states of Mn and Tc impurities in monovalent metal hosts, as obtained in non-spin-polarized jellium calculations (in eV).

Impurity \ Host	Cu	Ag	Li	Na	K	Rb	Cs
Mn	0.97	0.53	0.47	0.21	0.08	0.06	0.04
Tc	1.50	0.92	0.77	0.35	0.14	0.10	0.07

hibit the same qualitative features as their 3*d* counterparts. The important difference is, however, that the virtual bound states are considerably broader as a result of the stronger hybridization with the host. This result for the density of states of 4*d* impurities in alkali metals differs from the picture given in Ref. 25 for Mo in Na. There, an appreciable crystal-field splitting between the Mo d-e_g and d-t_{2g} states is shown which is absent in the present calculations. The reason for this discrepancy is an artifact in the previous construction of the host Green's-function elements of Na. This construction was based on a Kramers-Kronig integration over the imaginary part of the host Green's-function elements using a cutoff energy. Since the d-e_g and d-t_{2g} states of Na behave very differently near the chosen cutoff energy, the real part of the *d* Green's-function elements was calculated to be much different, leading to the different energy positions of the Mo *d* states. The present calculations use the direct Brillouin-zone integration over the reciprocal KKR matrix (for a comparison with the Kramers-Kronig integration, see Ref. 31). This direct integration leads to much more reliable Green's-functions for the alkali metals. The d-e_g and d-t_{2g} elements are very similar, and the calculated crystal-field splitting of the impurity *d* states is very small, in agreement with the results of Ref. 19.

As a typical example of our results, the widths of the virtual bound states for a 3*d* impurity (Mn) and an isoelectronic 4*d* impurity (Tc) in the different hosts are summarized in Table I. These results refer to jellium calculations without spin polarization. Between the Cu and Cs hosts, the width of the virtual bound state dramatically decreases by about a factor 20. Thus the host density is the most important parameter, compared to which the difference between the 3*d* and 4*d* impurities is of minor importance. It clearly shows that in the heavier alkali metals the 3*d* and 4*d* impurities are quite close to the atomic limit.

B. Local moments

The local impurity moments M_{loc} in Cu, Ag, Li, Na, and K hosts are shown in Figs. 3 and 4 together with the jellium results, as a function of the reduced free-electron density of the host $\bar{\rho}/\bar{\rho}_c$. A more detailed account of the impurity moments in the different hosts is given Table II for the 3*d* impurities and Table III for the 4*d* case. The dilute limit $\bar{\rho}=0$ corresponds to local-density-functional

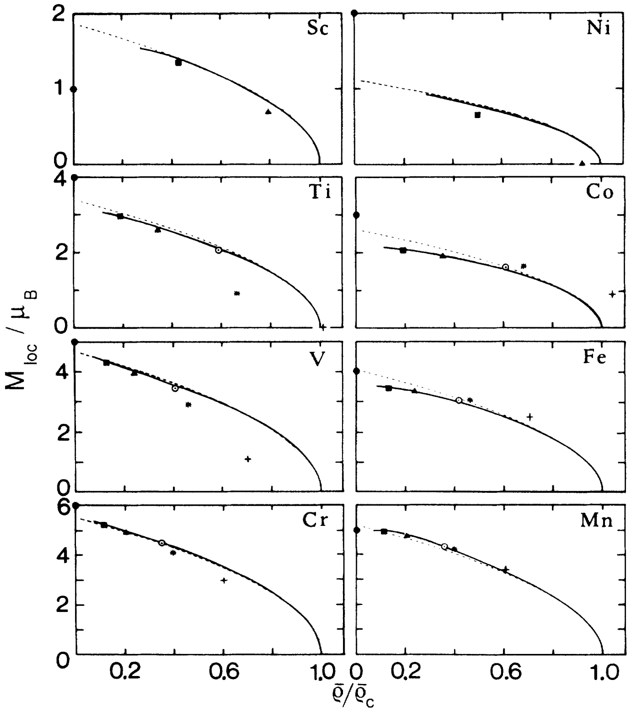

FIG. 3. Local moments of 3*d* impurities in jellium (solid curve). The dashed curve refers to the result of the interpolation formula (1). The symbols +, ∗, ⊙, △, and □ show the KKR results in Cu, Ag, Li, Na, and K hosts, respectively. The dots (for $\bar{\rho}=0$) represent the atomic spin moments (Ref. 29).

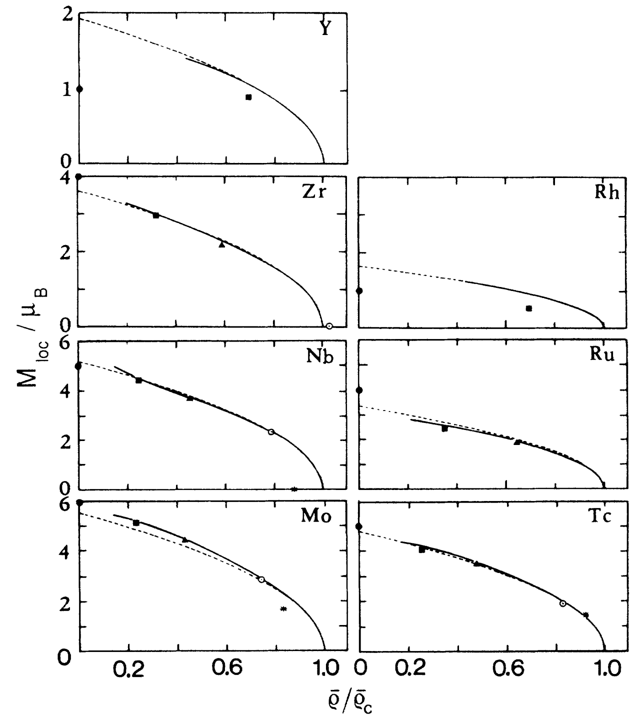

FIG. 4. Local moments of 4*d* impurities. The nomenclature is the same as in Fig. 3. The Pd atom does not exhibit a spin moment.

TABLE II. Local spin moments of 3*d* impurities in monovalent hosts as calculated in the local-spin-density approximation. The results have been obtained by the KKR–Green's-function method, except for the Rb and Cs hosts for which only jellium calculations have been performed ($\times\mu_B$).

Impurity Host	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Cu	0	0	1.09	2.99	3.40	2.51	0.89	0
Ag	0	0.92	2.90	4.09	4.20	3.06	1.65	0
Li	0	2.07	3.47	4.47	4.33	3.06	1.61	0
Na	0.69	2.59	3.93	4.90	4.72	3.33	1.93	0
K	1.36	2.96	4.29	5.20	4.90	3.43	2.06	0.65
Rb	1.50	3.06	4.44	5.35	4.98	3.47	2.14	0.86
Cs	1.54	3.07	4.50	5.40	4.96	3.48	2.15	0.91

calculations for the free atom.[29] The corresponding atomic moments are indicated by black dots. As can be seen, the atomic spin moment cannot be obtained in most cases by smoothly extrapolating the calculated results for the impurities embedded in a free-electron gas. This is due to the fact that the distribution of the electron states changes rapidly as the atomic limit is approached.[21] Note that the moments listed in Tables I and II also contain contributions from *sp* electrons (see below).

The agreement between KKR and jellium results for the impurity moments in alkali metals is very good. However, in the noble-metal hosts Cu and Ag, the jellium calculations overestimate the local moment of the early 3*d* and 4*d* impurities, whereas the moment of the late transition elements is somewhat underestimated. This can be explained by the *d*-*d* hybridization between the impurity virtual bound state and the low-lying host *d* states, which is not included in the jellium model. The situation is illustrated in Fig. 5, where we compare KKR with jellium results for non-spin-polarized local densities of states of V, Cr, Mn, and Fe impurities in Cu. The *d*-*d* hybridization pushes the impurity virtual bound state to higher energies. As a result, for an impurity with a less than half-filled *d* shell, e.g., V, $n_{\text{loc}}(E_F)$ decreases. In addition, the *d*-*sp* hybridization between the impurity virtual bound state and the host free-electron gas becomes stronger, the virtual bound state is broadened, and $n_{\text{loc}}(E_F)$ is further reduced. This finally leads to a smaller magnetic moment, according to the criterion of Blandin and co-workers, than obtained in the results of a jellium calculation. On the other hand, for an impurity with a more than half-filled *d* shell, i.e., Mn or Fe, the increase of $n_{\text{loc}}(E_F)$ due to the shift of the virtual bound state to higher energies is partly counterbalanced by the broadening of this state induced by the stronger *d*-*sp* hybridization. The competition of these two effects leads finally to a slight underestimation of the impurity moment in the jellium calculation. Note that the discrepancy between KKR and jellium results is larger in Cu than in Ag, because the *d* band of Ag is lower in energy and correspondingly the *d* electrons are more strongly localized, so that the *d*-*d* hybridization is weaker. Therefore the jellium results are somewhat more appropriate for Ag than for Cu.

In the vicinity of the transition from a spin-polarized to a non-spin-polarized impurity state, the local moment varies as[32]

$$M_{\text{loc}}=M_0(1-\bar{\rho}/\bar{\rho}_c)^{1/2} \; . \tag{1}$$

This expression is very similar to the result of the Landau theory for second-order phase transitions and also applies for jellium densities farther away from the critical point. The dashed lines in Figs. 3 and 4 represent this approximation with M_0 determined by the behavior of M_{loc} close to the critical density $\bar{\rho}_c$. According to Eq. (1), the local moment increases in a relatively small range of densities $\bar{\rho}_c \geq \bar{\rho} \geq \frac{3}{4}\bar{\rho}_c$, from zero to half the saturation value, i.e., $M_0/2$. We expect therefore uncertainties arising from the local spin-density approximation to be restricted to densities $\bar{\rho}$ close to $\bar{\rho}_c$.

According to the criterion of Blandin and co-workers, favorable conditions for the occurrence of a local moment are a large exchange integral and a high impurity local density of states at E_F. In a very dense jellium where the impurity virtual bound state is too much broadened, the criterion of Blandin and co-workers is not

TABLE III. Local spin moments of 4*d* impurities in monovalent hosts. The results have been obtained by the KKR–Green's-function method, except for the Rb and Cs hosts for which only jellium calculations have been performed ($\times\mu_B$).

Impurity Host	Y	Zr	Nb	Mo	Tc	Ru	Rh	Rd
Cu	0	0	0	0	0	0	0	0
Ag	0	0	0	1.67	1.44	0	0	0
Li	0	0	2.33	2.90	1.97	0	0	0
Na	0	2.18	3.67	4.40	3.46	1.85	0	0
K	0.89	2.95	4.38	5.10	4.04	2.41	0.51	0
Rb	1.27	3.16	4.70	5.34	4.31	2.71	1.09	0
Cs	1.40	3.27	4.93	5.42	4.37	2.82	1.23	0

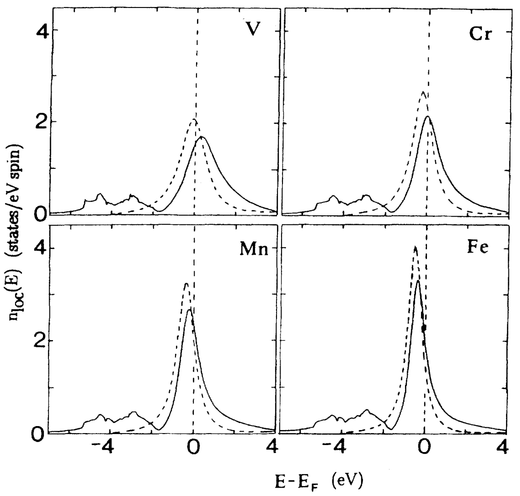

FIG. 5. Non-spin-polarized impurity local density of states for V, Cr, Mn, and Fe impurities in Cu [KKR (solid curve) and jellium (dashed curve)].

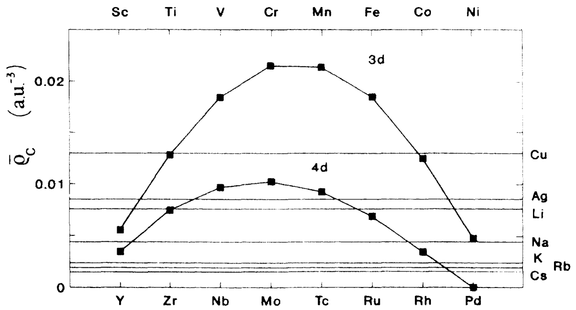

FIG. 6. Critical densities of jellium host, $\bar{\rho}_c$, below which the impurity becomes magnetic. The parallel lines to the abscissa correspond to the jellium densities of (from up to down) Cu, Ag, Li, Na, K, Rb, and Cs.

satisfied. This criterion starts to apply at a critical jellium density $\bar{\rho}_c$, below which a local impurity moment is formed. The variation of $\bar{\rho}_c$ for the transition-metal impurities is shown in Fig. 6. Both curves for the 3*d* and 4*d* impurities exhibit a similar parabolic behavior with a maximum in the middle of the series. The small shift of the curve for the 4*d* elements to the left can be explained by the fact that the *d* shell of the late 4*d* impurities has more electrons compared to their 3*d* counterparts (see below).

Physically, the most important difference between 4*d* and 3*d* impurities is the somewhat larger spatial extent of the 4*d* wave function, which leads to a stronger hybridization with the host and to a slightly smaller exchange integral. Both facts are unfavorable for spin polarization and represent the basic reasons why 4*d* metals and the corresponding alloys are normally nonmagnetic. As a further consequence, 4*d* impurities become magnetic only at more dilute jellium densities than their 3*d* counterparts, as is illustrated in Fig. 6. Within a given series, the condition for magnetism is most likely to be met when the virtual bound state is close to the Fermi energy, since the exchange integral does not vary strongly within the series. Therefore impurities with a half-filled *d* shell, i.e., Cr, Mn or Mo, Tc, show the strongest tendency to spin polarization and thus become magnetic in a wider range of jellium densities and have the largest local moments in a given simple-metal host. This is confirmed by our calculations. As can be seen from Fig. 6, the $\bar{\rho}_c$ curve for the 4*d* series is slightly shifted to lower valencies as compared with the corresponding 3*d* curve. This is basically caused by the shift of the atomic 5*s* level of the 4*d* atoms to higher energies, leading to smaller *s* counts and larger *d* counts in the 4*d* series as compared with the 3*d* one. This explains why the maximum of the $\bar{\rho}_c$ curve occurs in the 4*d* series at Nb and Mo as compared with Cr and Mn in the 3*d* series and why Pd does not become magnetic even in K, Rb, or Cs (even a free Pd atom has a zero spin moment), whereas Ni is strongly magnetic (see below). From the behavior of the $\bar{\rho}_c$ curves for the 3*d* and 4*d* impurities, one might guess that also impurities of the 5*d* series should become magnetic in these exotic hosts. Thus we believe that the substitutional 5*d* impurities from the middle of the series are magnetic in the heavier alkali hosts. This is also indicated by the half-widths of 3*d* and 4*d* impurities listed in Table I, which suggests similar small values also for 5*d* impurities.

It is noteworthy that the results for $\bar{\rho}_c$ as given in Fig. 6 are rather insensitive with respect to the exchange-correlation potential used. For instance, for a Mo impurity the critical value ρ_c is (in 10^{-2} a.u.$^{-3}$): 1.01 for the potential of Moruzzi *et al.* [29], 0.98 for the Vosko-Wilk-Nusair potential [30] and 0.95 for the one of von Barth and Hedin [28]. This is in agreement with the general experience that, except for critical cases, the special form of the exchange-correlation functional influences the results only slightly.

C. Formation of local *s* moments

From Tables II and III, as well as Figs. 3 and 4, one sees that the moments of Cr and Mo in the heavier alkali metals exceed the limit of $5\mu_B$, the maximal *d* moment possible. The reason for this is that under such dilute conditions the transition-metal impurities also develop a sizable *s* moment, as naturally occurs for the free atoms. This can also be seen from the local density of states of the 3*d* impurities in Li and K, as shown in Figs. 1 and 2. At the bottom of the majority subband, a second smaller peak occurs, corresponding to a nearly bound impurity *s* state. This peak can also be observed in the density of states of the neighboring host atoms, indicating the large extent of this orbital. The corresponding 4*s* peak in the minority band is shifted to higher energies and is strongly broadened, so that it can hardly be seen. Thus there also exists a significant exchange splitting of the *s* levels, a feature which has not been previously observed in local moment calculations.[10–20]

A detailed account for the formation of the *s*, *p*, and *d* moments is given in Table IV for the 3*d* impurity Cr. In the noble metals, the non-*d* components of the moments

TABLE IV. Angular momentum decomposition of the local moment of a Cr impurity in monovalent metal hosts ($\times\mu_B$) according to KKR and jellium (for Rb and Cs) calculations.

	Cu	Ag	Li	Na	K	Rb	Cs
s	0.03	0.06	0.09	0.18	0.26	0.36	0.40
p	0.03	0.06	0.09	0.12	0.16	0.14	0.11
d	2.93	3.97	4.29	4.60	4.78	4.85	4.89
Total	2.99	4.09	4.47	4.90	5.20	5.35	5.40

are very small, typically $0.01\mu_B$. However, already in Na, sizable s and p moments develop, e.g., about $0.18\mu_B$ and $0.12\mu_B$ for the Cr impurity. Because of the strong decrease of the Fermi energy of the host, the s moment of Cr then further increases to $0.40\mu_B$ in Cs, whereas the p moment slowly increases to $0.16\mu_B$ in K, and then decreases to $0.14\mu_B$ in Rb and $0.11\mu_B$ in Cs. This behavior is to be expected since in the atomic limit (configuration $3d^5\,4s^1$) the p moment vanishes, whereas the s moment is $1\mu_B$. Similar sp moments are also calculated for $4d$ impurities; e.g., for a Mo impurity an s moment of $0.37\mu_B$ is obtained in Rb and $0.41\mu_B$ in Cs. Thus, for the systems considered, we have a twofold transition to the atomic limit, the one for the d electrons, which is essentially completed already for Na or K, and the one for the s and p levels, which we just begin to notice at Cs. This is, of course, a direct consequence of the much larger spatial extent of the s and p wave functions. For this reason we also expect that in contrast to the d moments the s and p moments react sensitively to lattice relaxations and might be considerably reduced on interstitial positions.

IV. COMPARISON WITH EXPERIMENTS

The experimental information for the local moments of $3d$ impurities in noble-metal hosts arises from measurements of bulk susceptibility,[33] neutron-scattering cross section,[34] and study of the de Haas–van Alphen[35] and Mössbauer effects,[36] as well as various electron-spectroscopy measurements.[37] Detailed comparison of the calculated moments with the experimental values has been reported elsewhere,[11,12] and in general the agreement is satisfactory.

Recently, the variety of host materials has been extended to include alkali metals by the work of Riegel and coworkers[22,24–26] and Kowallik *et al.*,[23] who applied the time-differential perturbed γ-ray distribution method to investigate the local magnetic behavior of $3d$ and $4d$ impurities implanted by recoil into the host crystal. Alkali metals provide a wide range of free-electron densities, and thus one can closely study the transition of the d impurities from itinerant to atomic configurations. The calculated KKR local moments in alkali-metal hosts agree very well with the corresponding jellium results, as expected, since in this case the valence electrons of the host can be adequately described by the jellium model.

In the case of an Fe impurity in alkali metals, our calculations yield local spin moments somewhat higher than those calculated by McHenry *et al.*[19] This is presumably due to the finite size of the cluster used in their calculations. Our value for the Fe impurity moment in late alkali metals corresponds to a nonintegral spin $S=1.75$, in satisfactory agreement with the experimental finding for strong $3d$ magnetism of Fe in K, Rb, and Cs. The calculated magnitude of the spin is consistent with the value $S=2$ resulting from the ionic-type analysis of Riegel *et al.*[22]

Experimental data are also available for a Ni impurity in alkali metals.[23] Our results confirm that Ni in Li is nonmagnetic. For Ni in the late alkali metals K, Rb, and Cs, we calculate local moments ranging from $0.7\mu_B$ to $0.9\mu_B$. These values correspond to a nonintegral spin ranging from 0.35 to 0.45, in good agreement with the fully localized spin-orbit-coupled $3d$ configuration ($S=\frac{1}{2}$, $L=2$, $J=\frac{5}{2}$) reported from the experiment.[23] In the Na host, it was found that the magnetic behavior deviates drastically from that of the pure ionic configuration. This is consistent with our calculation, which either converges to a nonmagnetic solution (KKR) or yields a small local impurity moment of $0.32\mu_B$ (jellium).

Contrary to the $3d$ elements, $4d$ impurities in nonmagnetic hosts do not usually carry a local moment. However, recent calculations by Willenborg, Zeller, and Dederichs[13] showed that Mo and Tc in Ag might have quite sizable local moments ($1.55\mu_B$ and $1.41\mu_B$, respectively), in agreement with our present results. It is expected that $4d$ impurities in alkali-metal hosts can have very large moments, especially in the heavier host elements, because of their extremely low electron density. Indeed, experimental findings[24–26] as well as our results strongly support this expectation.

For Mo in Na, K, Rb, and Cs, we calculate a nonintegral spin S ranging from 2.2 to 2.7, which is consistent with the values $S=\frac{5}{2}$ resulting from the ionic-type analysis for the $4d$ configuration with $L=0$ reported from experiment.[24–25]

The local magnetism of Tc and Ru ions in Rb and Cs has been also investigated experimentally.[26] Using an ionic-type analysis, the experimental data for Tc in Rb can be well reproduced by a mixture of the ionic Tc ($S=\frac{5}{2}$) and Tc ($S=2$) levels, whereas the magnetism of Ru in Rb and Cs can be explained by assuming a predominant $4d$ ($S=\frac{3}{2}$) state. The results of this analysis are consistent with the itinerant picture of our calculation, which yields local spin values of 2.2 and 1.4 for Tc and Ru impurities in the late alkali metals, respectively. In the thesis of Gross,[26] also the behavior of $4d$ impurities from the beginning (Zr,Nb) and end (Rh,Pd) of the $4d$ series is examined. Nb and Rh in Rb and Cs show only a rather weak tendency for magnetism, and within the experimental uncertainties, Zr and Pd are nonmagnetic.

While the behavior of Pd is in line with our calculations, we obtain quite large moments for Zr and Nb in Rb or Cs, which makes the behavior of these impurities difficult to understand.

By comparing with the experiments, one should have in mind that the local-spin-density-functional calculations are unable to yield the large orbital moments which one expects from Hund's second rule and which have indeed been observed for the $3d$ and $4d$ impurities in the alkali-metal hosts. The formation of orbital moments in these simple-metal hosts and their suppression in the noble- and transition-metal hosts are challenging theoretical problems for future research.

In the late alkali hosts K, Rb, and Cs, Gross, Riegel, and Zeller proposed unusually large lattice contractions around d ions with localized d states, up to 22% for the extreme case of Fe in Cs. Consequently, our approximation of neglecting lattice relaxation in the calculation of the local moment is not *a priori* justified for these systems. In order to check the validity of this approximation, one should essentially examine the effect of the increase of hybridization between the impurity virtual bound state and the host free-electron gas, which results from lattice contraction around the impurity. Considerable enhancement of the impurity-host hybridization is achieved if the impurity occupies an interstitial rather than the substitutional position. Simplified calculations for interstitial impurities can also be performed by the jellium model. In this respect the impurity ion is superimposed to the jellium and not embedded in a spherical hole in the positive background (as done for substitutional impurities). The results show that for $3d$ impurities there is no dramatic change of the impurity moment, at least in the late alkali-metal hosts where the moment is more or less saturated. Typically, for an interstitial Fe impurity in Cs, we calculate a decrease of the local moment by $\cong 10\%$ compared with the results for the substitutional impurity. However, larger effects are expected in the lighter hosts or for $4d$ impurities. Detailed calculations are necessary.

V. CONCLUSION

We calculated the electronic structure of $3d$ and $4d$ substitutional impurities in simple and alkali-metal hosts self-consistently within the framework of local-spin-density-functional theory by using the KKR–Green's-function method and the jellium model. The results for the local magnetic properties of the impurity from both calculations are in good agreement and compare well with the available experimental data.

The close agreement of the jellium results with those obtained by the first-principles KKR–Green's-function method, especially in the case of alkali-metal hosts, shows that the jellium model provides an accurate description of the magnetic properties of the impurity. Because of the simplicity of the model, we can readily gain physical insight into the formation of local spin moments in simple-metal hosts. By continuously changing the jellium density, we have investigated for all substitutional $3d$ and $4d$ impurities the behavior of the local moments as a function of the density. Especially, we have determined the critical density at which magnetism sets in. With the exception of Pd, all impurities become magnetic in the heavier alkali metals. The widths of the virtual bound states decrease dramatically by reducing the jellium density, e.g., by a factor 20, between the Cu and Cs densities. Therefore the impurities exhibit in the late alkali metals an atomiclike behavior. In addition to the d moment, being more or less saturated in the heavier alkali metals, the calculations also yield a sizable s moment, showing that also the sp electrons experience the effect of localization.

There are two problems requiring substantial future work. Because of the large size differences between the impurities and alkali hosts, one expects very large lattice relaxations,[25] which are neglected in the present calculations. Also, off-center or interstitial positions might be of similar stability. The second problem concerns the occurrence of ionic configurations with atomic orbital moments which cannot be described in local-density-functional theory. Model calculations to describe such ionic effects will be published elsewhere.[38]

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