Can 5*d* and *sp* Impurities Be Magnetic?

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We present a systematic study of local spin moments of impurities in alkali-metal hosts, by means of *ab initio*, local-spin-density electronic structure calculations. Our results predict for the first time that besides the well-known cases of 3*d* and 4*d* impurities also 5*d* and some *sp* impurities are magnetic in the alkali metals both on substitutional and interstitial positions.

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As a general rule in the transition metals and transition-metal alloys magnetism is restricted to the 3*d* elements. For instance all elemental 4*d* and 5*d* metals are nonmagnetic in equilibrium. Only Pd and Pt at the end of the 4*d* and 5*d* series show a strong tendency towards magnetism with large Stoner enhancements. Also alloys or other metallic systems where 4*d* and 5*d* elements carry a magnetic moment are very rare. Interestingly Zhu, Bylander, and Kleinman [1], Erikkson, Abers, and Boring [2], and Blügel [3] have recently predicted sizable moments for 4*d* and 5*d* monolayers on noble metal surfaces.

In a series of experiments Riegel and co-workers [4] have recently demonstrated that 4*d* impurities implanted into alkali metals carry very large local moments as large as $5\mu_B$ for Mo in Rb and Cs. Obviously, the large volume available for the impurities in the alkali metals makes these atomlike moments possible. In a recent publication [5] we have performed detailed *ab initio* calculations for 3*d* and 4*d* impurities in monovalent simple-metal hosts and have elucidated the major trends for the formation of local moments of 3*d* and 4*d* impurities. Because of the large moments obtained for 4*d* impurities in the heavier alkali metals it is interesting to ask whether also other impurities which are usually nonmagnetic can have local moments in these exotic hosts. Here we report such calculations for 5*d* and *sp* impurities. To our surprise we find that 5*d* impurities are not only magnetic in the alkali metals, but have similar large moments as the 4*d* impurities, irrespective if they occupy substitutional or interstitial positions. As an even more astonishing result we predict that also the light *sp* impurities B, C, and N are magnetic, with *p* moments of about $(1.5\text{–}3)\mu_B$. Moreover there are indications that substitutional Si, P, Ge, and As impurities could be magnetic in Rb and Cs. It is the first time that local moments have been predicted for 5*d* and *sp* impurities, and we hope that the present results motivate experimental work to confirm these calculations and to study these interesting systems in more detail.

The theoretical electronic structure calculations of impurities in alkali-metal hosts were performed self-consistently within the framework of density functional theory [6], by using both the Korringa-Kohn-Rostoker (KKR) Green's function method [7] and the jellium model [8]. In the former method all band structure effects of the host are included and the embedding of the substitutional impurity into the host is properly described. On the other hand in the jellium model a free electron band structure is assumed and a substitutional impurity is created by excavating a spherical hole with the volume of the Wigner-Seitz cell in the positive background density and inserting the nuclear charge of the impurity in the center of the vacancy. Exchange and correlation effects are included in the calculations through the local-spin-density approximation of von Barth and Hedin [9] with the parametrization of Moruzzi, Janak, and Williams [10]. Relativistic effects for the 5*sp* and 5*d* impurities are taken into account within the scalar relativistic approximation [11]. Details about our calculational methods can be found elsewhere [7,8].

As a central result of our calculations Table I shows the calculated spin moments of substitutional 5*d* impurities in the various alkali hosts. Quite surprisingly the moments are similar and just as strong as those calculated for the corresponding 4*d* impurities [5]. Especially the moments of W and Re impurities approach in the heavier alkali metals, i.e., Rb and Cs, the saturation value of $5\mu_B$. Even in the Li host quite sizable moments are obtained for Ta, W, and Re. The very good agreement between KKR and jellium results justifies the use of the simple impurity-in-jellium model for the calculation of magnetic moments in these systems. Thus, not unexpectedly, band structure effects play a minor role.

As an advantage of the jellium model, the jellium density $\bar{\rho}$ can be varied continuously. In this way one can closely study the transition from the saturated atomic moments obtained for $\bar{\rho} \to 0$ to the suppression of the impurity moment for larger host densities. The moment vanishes beyond a critical density $\bar{\rho}_c$ and varies for smaller densities $\bar{\rho} \leq \bar{\rho}_c$ as $M \cong M_0(1-\bar{\rho}/\bar{\rho}_c)^{1/2}$ [8].

The critical densities $\bar{\rho}_c$ for the transition-metal impurities are shown in Fig. 1(a). The $\bar{\rho}_c$ results for the 3*d* and 4*d* impurities have been published earlier [5]. The surprisingly close proximity of the $\bar{\rho}_c$ curves for the 4*d*

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TABLE I. Local magnetic moments of $5d$ substitutional impurities in alkali metals as calculated by the KKR (jellium) method. For Cs only jellium calculations have been performed.

Impurity \ Host	Li		Na		Ka		Rb		Cs
Hf	0	(0)	1.31	(1.69)	2.20	(2.34)	2.32	(2.44)	(2.49)
Ta	1.50	(1.63)	3.12	(3.28)	3.77	(3.83)	3.86	(3.91)	(3.94)
W	2.41	(2.30)	4.17	(4.18)	4.83	(4.84)	4.94	(4.96)	(5.03)
Re	1.60	(1.37)	3.76	(3.59)	4.52	(4.40)	4.67	(4.51)	(4.59)
Os	0	(0)	2.17	(2.08)	2.89	(2.93)	3.06	(3.07)	(3.17)
Ir	0	(0)	0	(0)	1.17	(1.41)	1.49	(1.63)	(1.79)

and the $5d$ elements indicates that these two series of impurities have very similar magnetic behavior. This is quite different from the usual assumption that the magnetism in the $5d$ metals is even stronger suppressed than in the $4d$ ones. In contrast to this, the substitutional $3d$ impurities exhibit a much stronger tendency for spin polarization as can be seen from Fig. 1(a). We also observe that the $\bar{\rho}_c$ curve for the $4d$ elements is somewhat shifted to the left compared with that of the $3d$ ones. This is due to the fact that the d occupation number of the $4d$ impurities is larger than that of their $3d$ counterparts, because the $5s$ states are higher in energy than the $4s$ ones. This favors a higher d occupancy which results in a shift of the maximum of the curve. This is clearly an atomic effect and explains for instance why a free Pd atom has the

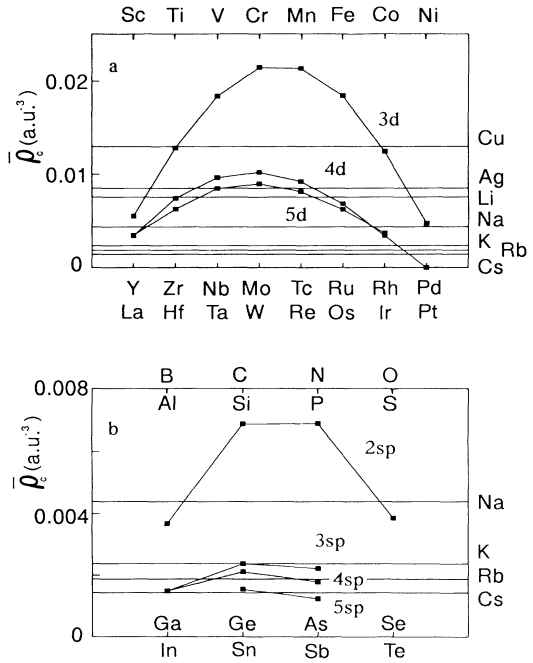

FIG. 1. Critical densities of jellium host, $\bar{\rho}_c$, below which each substitional d (a) and sp (b) impurity becomes magnetic. The lines parallel to the abscissa show the free electron densities of monovalent simple-metal hosts. Note that critical densities below 0.001 a.u.$^{-3}$ are not reported in the figure.

$4d^{10}$ configuration whereas its isoelectronic Ni has the $3d^8 4s^2$. For the same reasons one would expect that the $\bar{\rho}_c$ curve of the $5d$ impurities should be further shifted to the left. However, this does not occur. The reason is that for the $5d$ elements relativistic effects are rather important and they cause a shift of the $6s$ states back to lower energies. The two mechanisms almost cancel each other and therefore the $5d$ $\bar{\rho}_c$ curve is practically unshifted with respect to the $4d$ one.

The spin moments of the $5d$ impurities in K, Rb, and Cs are quite well saturated, as can be seen from Table I. This suggests almost atomic configurations for the $5d$ impurities in the late alkali-metal hosts, i.e., configurations with spin and orbital moments nearly as big as required by Hund's first and second rules for the free atoms. It is therefore reasonable to address the question whether there exist also magnetic sp impurities in these exotic hosts. For this reason we investigated also all the sp impurities at substitutional positions by means of self-consistent jellium calculations. Surprisingly, we find also many sp impurities to be magnetic in alkali-metal hosts. The results for the corresponding critical densities $\bar{\rho}_c$ are shown in Fig. 1(b). The calculated moments of these impurities in the various alkali metals are given in Table II. We clearly find that B, C, N, and O should be magnetic in the heavier alkali metals, if residing on substitutional sites. Even Si, P, Ge, and As substitutional impurities could be magnetic, if the moments are not quenched by lattice relaxation.

The most pronounced tendency for spin polarization is exhibited by the $2sp$ impurities due to the relatively strong localization of the $2p$ wave function. The degree of localization of the p wave function decreases abruptly from the $2sp$ to the $3sp$ series and then very slowly as we proceed to the next series. This behavior is analogous to that of the d impurities mentioned above. Similarly, the shift of the $\bar{\rho}_c$ curve to the left as we move towards the late sp rows of the periodic table has its origin to the shift of the corresponding states to higher energies, thus favoring the p vs s occupation. For the $5sp$ impurities this trend faces the competition of relativistic effects which, on the contrary, tend to place the $5s$ state lower in energy. As a result, a further shift of the $\bar{\rho}_c$ curve is not observed for these elements.

TABLE II. Local magnetic moments of $2sp$ and $5d$ substitutional (interstitial) impurities in alkali metals as calculated by the jellium model.

Impurity \ Host	Li		Na		K		Rb		Cs	
B	0	(0)	0	(0)	1.20	(1.40)	1.37	(1.72)	1.49	(1.94)
C	0	(0)	1.95	(0)	2.54	(2.15)	2.63	(2.43)	2.70	(2.64)
N	0	(0)	1.71	(0)	2.27	(1.25)	2.37	(1.53)	2.45	(1.73)
O	0	(0)	0	(0)	0.87	(0)	0.99	(0)	1.07	(0)
Hf	0	(0)	1.69	(2.39)	2.34	(3.03)	2.44	(3.14)	2.49	(3.21)
Ta	1.63	(0.73)	3.28	(3.57)	3.83	(4.32)	3.91	(4.44)	3.94	(4.51)
W	2.30	(0)	4.18	(3.60)	4.84	(4.83)	4.96	(5.04)	5.03	(5.17)
Re	1.37	(0)	3.59	(2.30)	4.40	(3.58)	4.51	(3.83)	4.59	(3.93)
Os	0	(0)	2.08	(0)	2.93	(2.00)	3.07	(2.28)	3.17	(2.50)
Ir	0	(0)	0	(0)	1.41	(0)	1.63	(0.53)	1.79	(0.99)

We also examined the influence of the approximation used for the exchange-correlation functional to our results. For instance by using the exchange-correlation potential of Vosko, Wilk, and Nusair [12], instead of that of Moruzzi, Janak, and Williams [10] the results for the critical densities are affected only by a few percent.

The large size differences between the impurity and the large volumes of the alkali metals lead to unusually large lattice relaxations of the neighboring atoms. Based on the ionic model Gross and co-workers [4] predict an inward relaxation of 22% for substitutional Fe impurities and 9% for Mo impurities in Cs. Somewhat smaller relaxations are expected for $5d$ impurities. One could argue that the large relaxations would strongly reduce or even quench the moments. For the following reasons this is, however, not the case. First, the spin polarization energies are very large, e.g., about 2 eV for W in Rb, leading to very stable moments. This is, e.g., quite different from the situation of $4d$ and $5d$ monolayers [1–3], which have spin polarization energies of a few mRy only and which therefore might react sensitively to lattice relaxations. Second, the effect of local relaxations can be simulated by a homogeneous compression being realized in nature by the different lattice constants of the alkali metals. However, even in Li, the lattice constant of which is 42% smaller than the one of Cs, sizable moments are calculated. Third while $4d$ and $5d$ impurities have very similar moments, the larger relaxations of the $4d$ impurities do not strongly affect the moments, as experiments show [4].

Recently strong evidence has been reported that in addition to substitutional positions $3d$ and $4d$ impurities can also occupy interstitial configurations [4,13]. Thus it is important to investigate the size of the local moments for interstitial configurations. Because of the stronger hydridization one might expect the moments to be decreased or quenched completely. Such calculations for interstitial positions can be carried out rather easily by the jellium model. In this case, one has just to superimpose the nuclear charge of the impurity atom to the jellium background charge, instead of putting the impurity at the center of a spherical cavity in the positive background. The calculated local moments within the volume of a host atomic sphere around the impurity are listed in Table II, both for the interstitial and the substitutional position. As can be seen from these results the local moments of the $5d$ and $2sp$ impurities in the late alkali metals are quite stable and surprisingly insensitive against configurational changes, at least in a first approximation. The basic reason for this is that the moments are more or less saturated. Large effects occur only for hosts with jellium densities close to the critical density $\bar{\rho}_c$ of the corresponding impurities. For instance in the Na host C and N impurities lose their moments. Moreover all $3sp$ and $4sp$ impurities are nonmagnetic on interstitial sites, even in the heavier alkali metals. In total, however, the differences are rather small.

Nevertheless, a closer look reveals interesting differences in the magnetic behavior for the two configurations, which arise mainly from two different effects. First as a result of the stronger impurity-host hybridization in the interstitial case the impurity virtual bound state is broadened. Second, there are more electrons around an interstitial impurity than a substitutional one if we refer to the same volume. This can be easily understood within the jellium model, where the electrons have to screen, in addition to the impurity nuclear charge, also the jellium positive background which is removed in the case of a substitutional impurity. One might also interpret this as a large charge transfer to the interstitial impurity which typically amounts to about 0.7 electrons. Therefore, the virtual bound state of the interstitial impurity is shifted to lower energies in order to accommodate more electrons. This is shown in Fig. 2, where the results of a non-spin-polarization calculation for the local density of states (LDOS) of a C impurity in K at substitional and interstitial position are plotted together with the spin-polarized LDOS.

For interstitial impurities with a more than half-filled

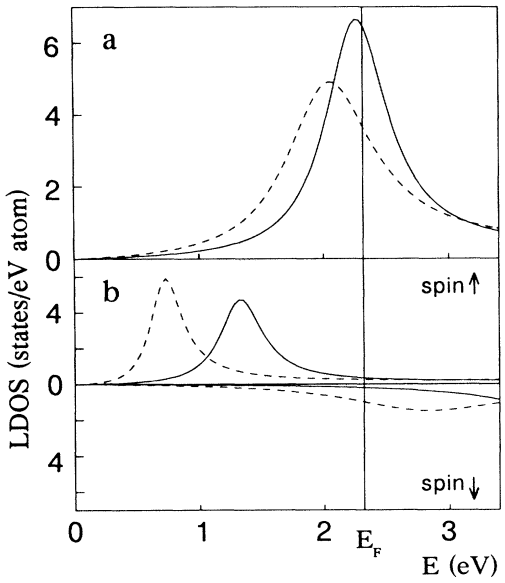

FIG. 2. LDOS of a C impurity in K jellium at substitutional (solid curve) and interstitial (dashed curve) position, both for the paramagnetic (a) and the spin-polarized (b) calculation.

resonant state, both effects discussed above lead to a strong decrease of the paramagnetic LDOS at E_F. Therefore, the interstitial impurity moment drastically decreases according to Blandin's criterion [14]. This can be clearly seen from Table II. For instance the moments of the N and O impurities are reduced, by about 1 μ_B in the case of N and totally quenched for O on interstitial configurations. In contrast to this, for impurities with a less than half-filled virtual bound state, the broadening of the resonance tends to decrease the LDOS at E_F, whereas its inward shift tends to increase it. This competition finally leads to a moderate increase of the impurity moments in the first half of the 5*d* series, as can be seen from Table II. Thus there are very important and characteristic differences between the two configurations.

In summary we have presented two new classes of local moment systems. Our *ab initio* calculations yield very large local moments for 5*d* impurities in alkali metals, being more or less saturated in K, Rb, and Cs and being similar in size to the moments found for 4*d* impurities, which are experimentally well established. The jellium calculations yield similar large moments also for the interstitial positions, with small but significant differences arising from the large charge transfer to the interstitial impurities. Quite sizable moments between $1.5\mu_B$ and $3\mu_B$ are also predicted for the light *sp* impurities B, C, and N, both for the interstitial and substitional configuration. Even Si, P, Ge, and As impurities could be magnetic on substitutional sites in the heavier alkali hosts. We hope that the present work will motivate experimental efforts to study these new and exotic systems.

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