

Magnetic Impurities in Simple Metals

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Abstract

The local magnetic behaviour of impurities in simple monovalent metal hosts is studied systematically by means of *ab-initio*, local-spin-density-functional electronic structure calculations. Our results predict that besides the 3*d* and 4*d* impurities also the 5*d* and some *sp* impurities are magnetic in the late alkali metals and that local magnetism can exist for impurities not only on substitutional but also on interstitial sites.

1. Introduction

The presence or absence of a magnetic moment of an impurity diluted in a nonmagnetic metal host is determined by a competition between intra-atomic exchange interaction and interatomic electron motion. Within the framework of the models of Anderson [1] and Wolff [2] the impurities are distinguished as magnetic and nonmagnetic according to the ratio of two parameters, the mean intra-atomic Stoner exchange energy I and the width Δ of the impurity virtual bound state. Blandin *et al.* [3] proposed a simple quantitative form for the condition for the occurrence of a local spin moment: $I \cdot n(E_F) > 1$. This condition is very similar to Stoner's criterion for band ferromagnetism. The only difference is that $n(E_F)$ here is the paramagnetic local density of states of the impurity at the Fermi level. Recently, Stefanou and Papanikolaou [4, 5] studied extensively the magnetic behaviour of impurities in jellium by means of self-consistent local-spin-density-functional calculations. They found that, in the vicinity of the transition from a spin-polarised to a non-spin-polarised impurity state, the local moment varies proportionally to $\sqrt{1 - \rho/\rho_c}$ for $\rho < \rho_c$. This expression is very similar to the result of the Landau theory for second-order phase transitions and, as it turns out, it also applies to jellium densities ρ away from the critical point ρ_c . Nowadays, new and more detailed information on the magnetic properties of impurities is emerging from the application of self-consistent computational formalisms developed in recent years [6–12].

The experimental investigations of the magnetic properties of impurities diluted in simple metals were for many years restricted to 3*d* impurities in noble metals and aluminum. Recently, the variety of host materials was extended to include alkali metals by the work of Riegel *et al.* [13], who applied the time-differential perturbed γ -ray distribution method to investigate the local magnetic behaviour of 3*d*

and 4*d* 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 impurities from itinerant to atomic configurations.

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 Korringa–Kohn–Rostoker- (KKR-) Green's function method in order to investigate the local magnetic properties of all the *sp* and *d* impurities in simple monovalent metal hosts.

2. Method of calculation

The theoretical electronic structure calculations of impurities in simple-metal hosts were carried out self-consistently within the framework of density functional theory [14] by using both the KKR-Green's function method [7] and the jellium model [4]. 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. Within this model, a substitutional impurity is created by excavating a spherical hole having the volume of the Wigner–Seitz cell in the positive background density and inserting the nuclear charge of the impurity in the centre of the cavity. Exchange and correlation effects are included through the local-spin-density approximation of von Barth and Hedin [15] with the parametrization proposed by Janak [16]. Relativistic effects for the 5*sp* and the 5*d* impurities are taken into account within the scalar relativistic approximation [17]. Details about our computational methods can be found elsewhere [4, 7].

3. Results and discussion

3.1. Critical densities

In this section we present results of systematic impurity-in-jellium calculations. In addition to substitutional impurities, which have been studied extensively in previous works [4, 9, 18], we also investigate here the magnetic behaviour of all the impurities in interstitial position. The jellium model has the advantage that the density ρ can be varied continuously.

Thus, one can closely study the transition from the saturated atomic spin moments ($\rho \rightarrow 0$) to the suppression of the impurity moment ($\rho = \rho_c$).

Within a given series of impurities, Blandin's criterion for magnetism is most likely to be met when the impurity virtual bound state is close to the Fermi energy, since the exchange integral does not vary strongly within a given series. Therefore, impurities with a half-filled shell show the strongest tendency for spin polarisation, thus becoming magnetic in a wider range of jellium densities. This is the reason why we find that the critical density curve in Fig. 1 has a parabolic-like behaviour within a given series, and the maximum is about in the middle of the series.

The surprising similarity of the critical density curves for the 4d and the 5d elements indicates that these two series of impurities have very similar magnetic behaviour. This is quite different from the usual assumption that the magnetism in the 5d metals is even more strongly suppressed than in the 4d ones. In contrast to this, the substitutional 3d impurities exhibit a much stronger tendency for spin-polarisation, as can be seen from Fig. 1. We also observe that the 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 favours a higher *d* occupancy which results in a shift of the maximum of the curve. This clearly is an atomic effect and explains for instance why a free Pd atom has the $4d^{10}$ configuration whereas its isoelectronic Ni has the $3d^8 4s^2$. For the same reasons one would expect that the curve for 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 relatively 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 curve is practically unshifted with respect to the 4d one.

Surprisingly, we find that besides the *d* magnetic impurities also many *sp* impurities are magnetic in alkali-metal hosts. The most pronounced tendency for spin-polarisation is exhibited by the 2*sp* impurities due to the relatively strong localisation of the 2*p* wave function. The degree of localisation of the *p* wave function decreases abruptly from the 2*sp* to the 3*sp* series, and then very slowly as we proceed to the next series. This behaviour is analogous to that of the *d* impurities mentioned above. Similarly, the shift of the critical density curve to the left as we move towards the late *sp* rows of the periodic table has its origin in the shift of the corresponding *s* states to higher energies, thus favouring the *p* versus *s* occupation. For the 5*sp* impurities this trend faces the competition of relativistic effects which, on the contrary, tend to place the 5*s* state lower in energy. As a result, a further shift of the curve is not observed for these elements.

The large size differences between the impurity and the large atomic volumes of the alkali metals might lead to unusually large lattice relaxations of the neighbouring atoms, as discussed by Riegel *et al.* [13]. Recently, strong evidence has been reported that in addition to substitutional configurations, transition-metal impurities can also occupy interstitial positions [19]. Thus, it is important to investigate the magnetic behaviour of impurities at interstitial configuration. Due to the stronger hybridisation, 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 centre of a spherical cavity in the positive background. The calculated critical densities for interstitial impurities are also shown in Fig. 1. Drastic changes of the local moments occur only for hosts with jellium densities close to the critical density of the corresponding impurities. For instance in Na host C and N impurities lose their

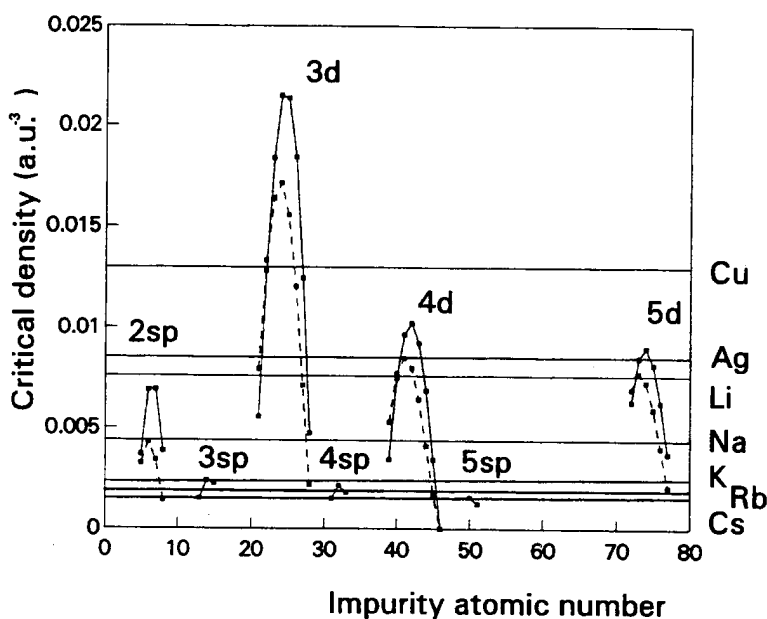


Fig. 1. Critical densities of jellium host below which each substitutional (full line) or interstitial (broken line) impurity becomes magnetic. The lines parallel to the abscissa show the jellium densities of monovalent simple-metal hosts. Note that critical densities below 0.001 au^{-3} are not reported in the figure.

moments when they are in interstitial positions. Moreover all 3*s*p and 4*s*p impurities are nonmagnetic on interstitial sites, even in the heavier alkali metals. In total, however, the differences are rather small and there is strong evidence for the existence of a new class of local-moment systems: interstitial impurities in heavy alkali metals.

3.2. Local moments and hyperfine fields

As we have shown [4, 9, 18], the agreement between KKR and jellium results for the impurity moments in alkali metals is very good. However, in the noble-metal hosts the jellium calculations overestimate the local moment of the early transition-metal impurities, whereas the moment of the late transition elements is somewhat underestimated. This is ascribed to the presence of the low-lying host *d* band, which is neglected in the jellium calculation as we have shown in previous works [4, 9]. The calculated impurity spin moments are in good agreement with the available experimental data. A detailed comparison has been reported elsewhere [9].

In the remaining part of the paper we shall discuss our results for the local magnetic properties (local moments and hyperfine fields) of substitutional impurities with a half-filled *d* shell, as calculated by the KKR-Green's function method. The magnetic moments of the transition-metal impurities with a half-filled *d* shell in the heavier alkali metals are quite large, with the *d* moments being practically saturated (see Fig. 2). The moments of Cr, Mo and W impurities in Rb for instance, even exceed the limit of $5\mu_B$, the maximum *d* moment possible. The reason for this is that under such dilute conditions the transition-metal impurities also develop a sizeable *s* moment, as it naturally occurs for the free atoms. This is illustrated in Table I, where the *s*, *p* and *d* contributions to the moment of Cr and Mo impurities in various hosts are given. In Li the non-*d* components of the moments are small. However, already in Na sizeable *s* and *p* moments develop, e.g. about $0.18(0.17)\mu_B$ and $0.13(0.11)\mu_B$ respectively for a Cr(Mo) impurity. Due to the strong decrease of the Fermi energy of the host, the *s* moment of Cr(Mo) then increases further to $0.40(0.41)\mu_B$ in Cs, whereas the *p* moment slowly increases to $0.16(0.18)\mu_B$ in K, and then decreases to $0.14(0.17)\mu_B$ in Rb and $0.11(0.15)\mu_B$ in Cs. This behaviour is expected since in the atomic limit (configurations: $3d^54s^1$ for Cr and $4d^55s^1$ for Mo) the *p* moment vanishes, whereas the *s* moment is $1\mu_B$. Thus, for the systems considered, we have a twofold transition as we approach the atomic limit: the one for the *d* electrons, which is essentially completed already in Na or K, and the other

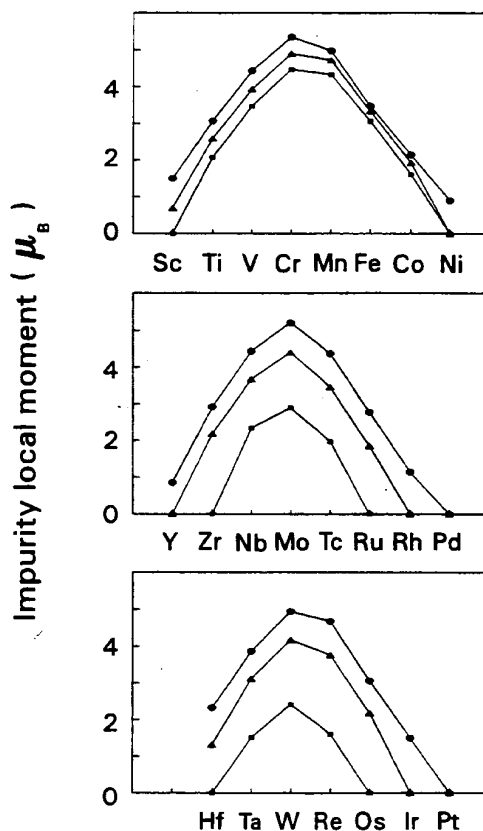


Fig. 2. Local moments of transition-metal substitutional impurities in Li (■), Na (▲) and Rb (●) hosts.

for the *s* and *p* levels which becomes noticeable in Cs. This is, of course, a direct consequence of the much larger spatial extent of the *s* and *p* wave functions.

The *s* moments are very important for the hyperfine fields of the impurities. The calculated hyperfine fields for Cr and Mo impurities are also listed in Table I, separately for the core and valence contributions. The core polarisation, which arises from the intra-atomic *s*-*d* exchange, is expected to vary linearly, but oppositely in sign, with the local *d* moment. This is confirmed by our calculations (see Table I). Unfortunately the core contribution is underestimated in the local spin density approximation by about 30% [20]. However here, the important point is that the formation of an *s* moment leads to a strong positive valence hyperfine field which, in the heavier alkali metals, cancels the negative core contribution so that the total hyperfine field becomes strongly positive. Due to the underestimation of the core

Table I. Angular momentum decomposition of the local moment of Cr and Mo impurities in alkali-metal hosts (units: μ_B), and hyperfine field (core and valence contributions) on the impurity (units: kG)

Host	Cr impurity				Mo impurity			
	Li	Na	K	Rb	Li	Na	K	Rb
M_s	0.10	0.18	0.26	0.29	0.06	0.17	0.26	0.30
M_p	0.11	0.13	0.16	0.14	0.04	0.11	0.18	0.17
M_d	4.24	4.58	4.77	4.82	2.84	4.14	4.64	4.74
M_{tot}	4.45	4.89	5.18	5.25	2.95	4.42	5.07	5.21
H_{core}	-453	-477	-487	-490	-644	-905	-985	-1000
H_{val}	447	620	753	825	633	1189	1526	1676
H_{tot}	-6	143	266	335	-11	284	541	676

field this might not happen in reality, so that relatively small negative or slightly positive values could be expected in cases such as Cr, Mo, W where no orbital moment exists.

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