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Magnetic 3d impurities in Nb and Mo revisited

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Abstract. We re-examine the electronic structure of 3d impurities in niobium and molybdenum using local density functional theory and an improved version of the KKR–Green function method. The calculations reveal an extraordinary sensitivity of the local 3d moments with respect to the angular momentum cutoff ℓ_{max} of the wavefunctions. Whereas previous calculations with $\ell_{max} = 2$ yielded very large moments for Cr, Mn and Fe impurities in Nb, these moments are completely suppressed, if higher angular momenta ($\ell_{max} = 3$ or 4) are added. A qualitatively similar trend is found for the Mo host; however the reduction of the local moments is more moderate. The present results are in good agreement with the experimental data.

1. Introduction

In the pioneering work of Matthias *et al* [1] and Clogston *et al* [2] it was found that Fe impurities are magnetic in molybdenum, but non-magnetic in niobium. This was one of the first times that the occurrence of local moments in non-magnetic matrices had been observed, which then was theoretically explained by the Anderson model [3]. A few years ago [4, 5] we presented *ab initio* calculations for the electronic structure of 3d impurities in Mo and Nb, which were based on a multiple scattering Green function method. Contrary to the experimental results [1, 2] these calculations yielded sizeable moments for Cr, Mn as well as Fe impurities in Nb. In view of the success of density functional theory in describing the magnetism of transition metals, the situation was quite puzzling and the disagreement between experiment and theory was not understood. The experimental findings of Matthias *et al* [1, 2] were recently confirmed by Riegel *et al* [6, 7] who implanted Fe into a whole series of simple and transition metals and measured the local susceptibility and the spin rates of the Fe impurities. The authors found that Fe impurities are non-magnetic in the group VB metals V, Nb and Ta, but magnetic in Cr, Mo and W (group VIB).

These new data motivated us to re-examine these systems using an improved version of the KKR–Green function method. The basic question is whether or not density functional theory in the local density approximation is able to describe the breakdown of the local Fe moment in Nb. Whereas the previous calculations used angular momenta up to $\ell_{max} = 2$ and included only the impurity potential [4] or in addition also the potentials of the first nearest-neighbour host atoms [5] into the self-consistency process, the present calculations take into account angular momenta up to $\ell_{max} = 3$ or 4 and perturbed potentials for five shells of host atoms. While the inclusion of more shells does not significantly change the previous results, the

calculations surprisingly turn out to be extremely sensitive with respect to the angular momentum cutoff ℓ_{max}. For instance, a $\ell_{max} = 2$ calculation yields a large local moment of $3.18\mu_B$ for Fe in Nb. In contrast to this, for $\ell_{max} = 3$ or 4 this moment is completely quenched, in agreement with the experiments [1,2,6,7]. The reason for this and the general trends obtained for all 3d impurities in Nb and Mo will be discussed in this paper.

The application of density functional theory to local moment systems is not unproblematic. Due to its emphasis on the single-particle density and magnetization, density functional theory has the character of a mean-field approximation, being qualitatively similar to the Hartree–Fock approximation of the Anderson model. Therefore the transition from a magnetic impurity to a non-magnetic one is sharp whereas due to fluctuations the transition is in reality continuous. For similar reasons density functional theory cannot describe the Kondo effect, i.e. the formation of the Kondo peak at the Fermi energy at low temperatures and the corresponding anomalies connected with it [8]. Despite these difficulties density functional theory is quite successful in predicting the behaviour of 3d impurities in solids. For instance, the calculated local moments for 3d impurities in noble metals [9] and in palladium [10] agree well with the values determined from susceptibility and neutron scattering measurements. The present paper shows that this is also true for Nb and Mo hosts. Moreover the host polarization induced by these impurities in Cu is directly comparable with Knight-shift satellite data of the Slichter group [11]. Practically all satellites are described well by the calculations and some wrong experimental assignments could be corrected.

2. Method of calculation

Our calculations are based on multiple scattering theory using the KKR–Green function method, which we will outline shortly for paramagnetic systems; the generalization to magnetic systems is obvious [9]. For a lattice of muffin-tin potentials centred at positions $\boldsymbol{R}^n$ the Green function can be expanded into eigensolutions of these spherically symmetric local potentials:

$$G(\boldsymbol{r}+\boldsymbol{R}^n,\boldsymbol{r}'+\boldsymbol{R}^{n'};E)=\sqrt{E}\delta_{nn'}\sum_L Y_L(\boldsymbol{r})H_\ell^n(r_>;E)R_\ell^n(r_<;E)Y_L(\boldsymbol{r}') + \sum_{L,L'} Y_L(\boldsymbol{r})R_\ell^n(r;E)G_{LL'}^{nn'}(E)R_{\ell'}^{n'}(r';E)Y_{L'}(\boldsymbol{r}'). \tag{1}$$

Here the vectors $\boldsymbol{r}$ and $\boldsymbol{r}'$ are restricted to the Wigner–Seitz cell and $r_>(r_<)$ denotes the larger (smaller) value of $r=|\boldsymbol{r}|$ and $r'=|\boldsymbol{r}'|$. The subscript $L=(\ell,m)$ denotes angular momentum numbers and $Y_L(\boldsymbol{r})$ are real spherical harmonics. The regular solution $[R_\ell^n(r;E)]$ and the irregular solution $[H_\ell^n(r,E)]$ of the radial Schrödinger equation for the nth muffin-tin potential are defined by their asymptotic behaviour outside the muffin-tin sphere of radius S, for $r \geqslant S$

$$\begin{aligned} R_\ell^n(r;E) &= j_\ell(\sqrt{E}r)+\sqrt{E}t_\ell^n(E)h_\ell(\sqrt{E}r) \\ H_\ell^n(r;E) &= h_\ell(\sqrt{E}r) \end{aligned} \tag{2}$$

where j_ℓ and h_ℓ are the spherical Bessel and Hankel functions and $t_\ell^n(E)$ is the usual on-shell t matrix for the nth potential.

All the information about the multiple scattering between the muffin-tins is contained in the structural Green function matrix $G^{nn'}_{LL'}(E)$. It can be related to its counterpart $\mathring{G}^{nn'}_{LL'}(E)$ for the host crystal by an algebraic Dyson equation:

$$G^{nn'}_{LL'}(E) = \mathring{G}^{nn'}_{LL'}(E) + \sum_{n'',L''} \mathring{G}^{nn''}_{LL''}(E)\Delta t^{n''}_{l''}(E)G^{n''n'}_{L''L'}(E). \qquad (3)$$

The summation goes over all sites n'' and angular momenta L'' for which the perturbation $\Delta t^{n}_{l''}(E) = t^{n''}_{l''}(E) - \mathring{t}^{\,n''}_{l''}(E)$ of the t matrices $\mathring{t}$ of the host is significant.

As perturbations we include the impurity potential and the potentials of five shells of host atoms. These 59 potentials are determined self-consistently in the framework of density functional theory. We use the local spin-density approximation of von Barth and Hedin [12] with the constants as given by Moruzzi *et al* [13].

For the angular momentum summations in equations (1) and (3) a cutoff at $\ell_{max} = 2, 3$ or 4 is used. The dependence of all quantities on ℓ_{max} is studied in detail and is of crucial importance for the results presented in this paper. The Green function matrix $\mathring{G}^{nn'}_{LL'}(E)$ for the host crystal is directly related to the band structure of the host. For details see [9]. Its imaginary part can be determined from the Bloch eigenfunctions and eigenvalues by an integration over a constant-energy surface, quite analogous to the calculation of density of states. The real part is obtained from the imaginary part by a Kramers–Kronig integration. The band structure of the host is generated from the potentials tabulated by Moruzzi *et al* [13], which are based on a self-consistent calculation with $\ell_{max} = 4$. In our calculations with $\ell_{max} < 4$ we use the same host potentials, being self-consistent for $\ell_{max} = 4$. The eigenfunctions are normalized for the new, i.e. smaller, ℓ_{max} value. In this way we effectively redistribute charge density contributions with $\ell > \ell_{max}$ onto the low angular momentum states $\ell \leqslant \ell_{max}$. For the Nb and Mo hosts these are typically 0.18 electrons for $\ell_{max} = 2$ and 0.03 for $\ell_{max} = 3$. While this is a rather small effect, which we thought to be unimportant up to now, we cannot fully exclude that part of the unusual ℓ_{max} dependence of the present results has its origin in this procedure.

3. Results and discussion

The sensitivity of the results with respect to the angular momentum cutoff ℓ_{max} is illustrated in tables 1 and 2, which show the local charges of Mn and Fe impurities in Nb (table 1) and in Mo (table 2) for different ℓ_{max} values ($\ell_{max} = 2, 3$ and 4). All values result from non-spin-polarized calculations. Two important features are observed. (i) There are no significant differences between the $\ell_{max} = 3$ and the $\ell_{max} = 4$ calculations. This is even more true for the Mo host, for which only the results for $\ell_{max} = 2$ and 3 are given. (ii) Considerable differences exist between the $\ell_{max} = 2$ and the $\ell_{max} = 3$ or 4 calculations, which are more pronounced for the Nb host. For instance for Fe (Mn) impurities in Nb, the local s charge decreases from 1.26 (1.15) electrons in an $\ell_{max} = 2$ calculation to 0.77 (0.74) for $\ell_{max} = 4$; i.e. by as much as 0.49 (0.41) electrons. About half of this charge is found back as an increase of the d charge which in both cases increases by about 0.2 electrons. The other half of the missing s charge is distributed on the local f and g states and on the neighbouring sites. In this way the charge transfer ΔQ is reduced. A qualitatively similar, but quantitatively smaller, effect is found for the Mo host. When we proceed

Table 1. Results of calculations without spin-polarization for Mn and Fe impurities in Nb using different angular momentum cutoffs ($\ell_{max} = 2, 3$ and 4). The numbers of s-, p-, d-, f- and g electrons of the impurity, the charge transfer ΔQ to the impurity and the local densities of states at the Fermi energy (in units of $(eV)^{-1}$) are given. All these quantities refer to the Wigner–Seitz sphere of the impurities.

	ℓ_{max}	s	p	d	f	g	ΔQ	$n_{loc}(E_F)$
Mn	2	1.15	0.97	5.68	—	—	0.82	2.28
	3	0.76	0.98	5.87	0.09	—	0.69	1.82
	4	0.74	0.97	5.87	0.09	0.03	0.70	1.80
Fe	2	1.26	0.99	6.69	—	—	0.94	1.91
	3	0.79	1.02	6.90	0.09	—	0.80	1.50
	4	0.77	1.02	6.90	0.09	0.03	0.80	1.43

Table 2. Same as table 1, but for Mn and Fe impurities in Mo. The results for $\ell_{max} = 2$ and 3 are given.

	ℓ_{max}	s	p	d	f	ΔQ	$n_{loc}(E_F)$
Mn	2	0.78	1.12	5.72	—	0.62	2.65
	3	0.73	0.99	5.79	0.11	0.62	2.45
Fe	2	0.81	1.15	6.77	—	0.73	4.72
	3	0.76	1.02	6.84	0.11	0.73	4.36

from $\ell_{max} = 2$ to $\ell_{max} = 3$, we redistribute about 0.18 sp electrons on the d and f states for both impurities in Mo, while the charge transfer ΔQ is unaffected.

For the magnetic properties the most important effect is the increase of the d charge in the $\ell_{max} = 3$ or 4 calculation. Figure 1 shows the local density of states of a Mn impurity (figure 1(a)) and Fe impurity (figure 1(b)) in Nb, as obtained from non-spin-polarized calculations with $\ell_{max} = 4$ (full curves) and $\ell_{max} = 2$ (broken curves). One clearly sees that in an $\ell_{max} = 4$ calculation the weight of the d density of states is shifted to lower energies, so that more d states are occupied. As a consequence of this the local density of states $n_{loc}(E_F)$ at the Fermi energy decreases significantly for both impurities. From table 1 one can see that this decrease is about 21% for Mn in Nb and 25% for Fe in Nb. For 3d impurities in Mo a similar, but smaller, decrease is observed which amounts to 8% for both Fe and Mn impurities.

Within the Anderson model [3] the condition for the occurrence of a local moment has the form of a Stoner criterium

$$I n_{loc}(E_F) > 1$$

where I is the exchange integral of the impurity and $n_{loc}(E_F)$ the local density of states of the impurity at E_F. Unfortunately in deriving this criterium one has either to assume that the impurity shows a well developed virtual bound state with Lorentzian lineshape or that the perturbation due to the impurity as well as the local moment is well localized in the impurity cell. Clearly for the considered cases neither a Lorentzian virtual bound state exists nor is the perturbation or the local moment well localized. Nevertheless the local density of states at E_F is intimately connected with the occurrence of a local moment, and in this way we interpret the appreciable decrease of $n_{loc}(E_F)$ in the present calculation as a strongly reduced tendency for magnetism. The following spin-polarized calculations support this interpretation.

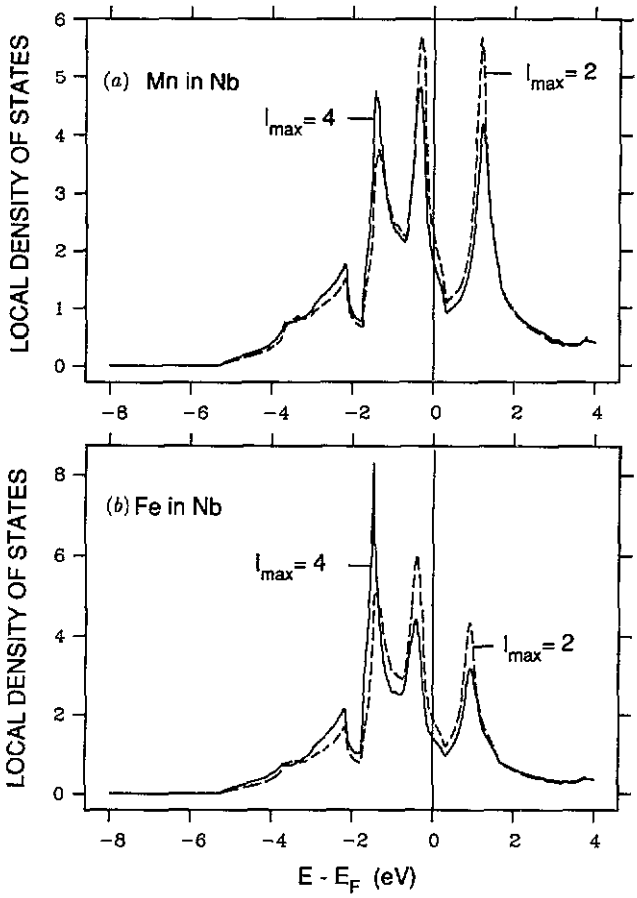

Figure 1. Local density of states of a Mn impurity (a) and a Fe impurity (b) in Nb according to a calculation without spin-polarization. Results for $\ell_{max} = 4$ (full curve) and $\ell_{max} = 2$ (broken curve) are shown.

For the Nb host these calculations exhibit a drastic dependence on the angular momentum cutoff ℓ_{max}. For $\ell_{max} = 2$ we obtain the following moments: $2.50\mu_B$ for Cr, $3.64\mu_B$ for Mn, $2.32\mu_B$ for Fe and $1.71\mu_B$ for Co impurities in Nb. These data are in good agreement with our previously reported results [5]. In contrast to this, in an $\ell_{max} = 3$ calculation the moments for Cr, Fe and Co are completely suppressed, whereas for Mn a rather small moment of $1.19\mu_B$ is obtained. This is further reduced to $0.37\mu_B$ in an $\ell_{max} = 4$ calculation (and would presumably vanish completely for $\ell_{max} = 5$). The present calculations are based on the exchange-correlation functional of von Barth and Hedin [10] but with the constants as proposed by Moruzzi and co-workers [13]. As discussed in [14] this functional has a somewhat larger tendency for magnetism then the local functional of Vosko *et al* [15] or the original one of von Barth and Hedin [12]. We have therefore repeated part of the present calculations with the exchange correlation functional of Vosko, Wilk and Nusair which is normally considered to be the best local functional, since it is determined from Monte Carlo results for the homogeneous electron gas. The resulting trend is very much the same: Fe and Cr impurities are non-magnetic and the moment of Mn impurities slightly

decreases to $0.35\mu_B$. Thus with the exception of Mn we find no moments for 3d impurities in Nb. Mn might have a very small moment and presumably represents a weak spin-fluctuation system.

Also in the Mo host the local moments of the 3d impurities are reduced if higher angular momenta are included in the calculation, however the decrease is much smaller. Both facts are in line with the trend shown by $n_{loc}(E_F)$ in calculations without spin-polarization (see table 2) where small decreases from much larger basis values are observed. The resulting local moments for $\ell_{max} = 2$ and 3 are given in table 3. Only Mn, Fe and Co have local moments, the values of which are about $0.9\mu_B$ smaller than the ones obtained with $\ell_{max} = 2$ [5]. The corresponding densities of states for both spin directions are shown in figure 2 for Mn and Fe impurities. As is typical for these systems the magnetism is strongly influenced by the covalent interactions [4] between the 3d orbitals of the impurity and the 4d ones of the host. Therefore no well defined virtual bound states exist which are, for example, characteristic for 3d impurities in the noble metals.

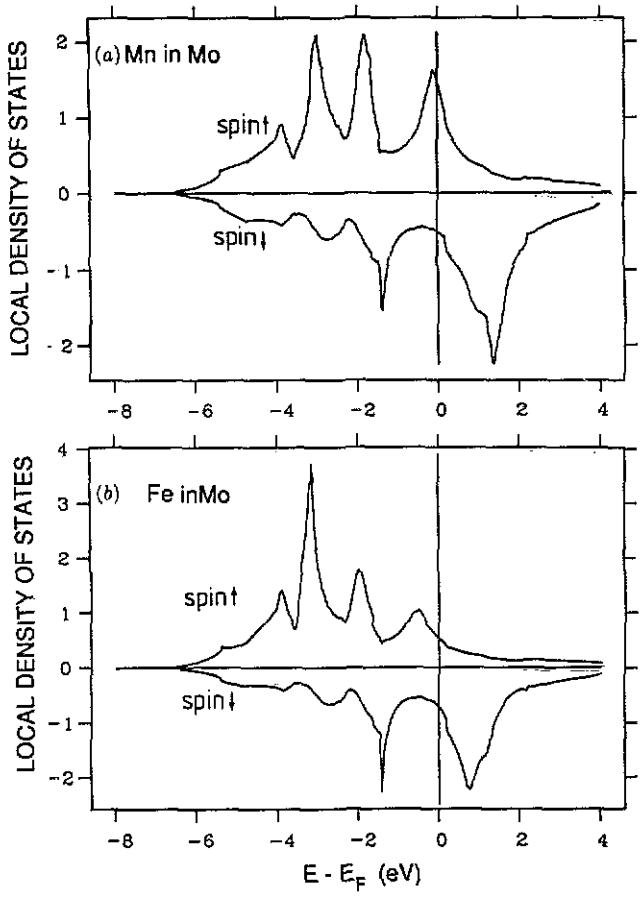

Figure 2. Local density of states for both spin directions for a Mn impurity (a) and a Fe impurity (b) in Mo. The angular momenta have been cut off at $\ell_{max} = 3$.

The strong ℓ_{max} sensitivity found for the 3d moments in Nb is quite unusual. We know of only one case where a similar sensitivity has been found: this concerns Mn

Table 3. Local moments of 3d impurities in Mo (in units of μ_B), according to calculations with $\ell_{max} = 2$ and 3 and five shells of perturbed host potentials around the impurity. Given are the local moment M_{loc} of the impurity, the moment M_{nn} of a nearest neighbour host atom and the total moment M_{tot} of the impurity and five shells of host atoms.

	ℓ_{max}	V	Cr	Mn	Fe	Co	Ni
M_{loc}	2	0	0	3.27	3.42	2.41	0
M_{loc}	3	0	0	2.32	2.51	1.52	0
M_{nn}	3	0	0	−0.01	0.05	0.07	0
M_{tot}	3	0	0	1.35	2.10	2.28	0

impurities in ferromagnetic Fe. Whereas Ni and Co impurities couple ferromagnetically to the host moments, the early transition metal impurities Ti, V and Cr align antiferromagnetically [16]. Mn is just at the borderline and the results sensitively depend on ℓ_{max}. By continuously varying the nuclear charge Z of the impurity, we find that for $\ell_{max} = 2$ the transition from ferromagnetic to antiferromagnetic coupling occurs at $Z = 25.04$, so that the Mn impurity (with $Z = 25$) has a negative moment, depending somewhat on the exchange correlation potential. On the contrary, for $\ell_{max} = 3$ this transition is shifted to a smaller nuclear charge $Z < 25$, and Mn gets a positive moment of $0.69\mu_B$, in agreement with experiments. The strong ℓ_{max} dependence found here for 3d impurities in Nb very probably has its origin in a similar instability. By changing the nuclear charge Z of the host, while retaining the bcc structure, the local moments presumably become quenched, if Z decreases below a certain critical value Z_c, which for $\ell_{max} = 2$ must be smaller than the nuclear charge 41 of Nb. In an $\ell_{max} = 3$ calculation this transition is apparently shifted to larger nuclear charges between Nb and Mo ($41 \leqslant Z_c \leqslant 42$) which would explain the calculated results. Such a behaviour is also suggested from the experimental results obtained for disordered NbMo alloys [2].

The present results for $\ell_{max} = 3$ or 4 are in good agreement with the experimental information. Since the pioneering work of Clogston *et al* [1,2] it is generally believed that 3d impurities are non-magnetic in Nb. No resistivity anomalies are found at low temperatures and the measured susceptibilities are rather flat. The more recent experimental work of Riegel *et al* [6,7] for Fe in Nb strongly support these results. It is therefore gratifying that, due to the improvements of the angular momentum expansion, this is also found in our calculations. Equally good agreement is found for the 3d impurities in Mo. From Mößbauer measurements at ^{57}Fe in Mo, Maley and Taylor [17] obtain a local moment of $2.6\mu_B$, which compares well with our value of $2.5\mu_B$. For the same system Anamou *et al* [18] obtain a somewhat larger value of $3.3\mu_B$. For the MoCo system measurements of Brog *et al* [19] yield a value of $1.6\mu_B$, compared to our value of $1.5\mu_B$. MoMn is a spin-glass system [20], but no definite value for the moment seems to be known. By contrast, Ni as well as Ti, V and Cr seem to be non-magnetic [21], in agreement with our calculations.

In summary, the present calculations show an extreme and unusual sensitivity of the local moments of 3d impurities in Nb with respect to the angular momentum cutoff ℓ_{max}. In contrast to previous results with $\ell_{max} = 2$, the local moments are completely suppressed if higher angular momenta are included. For the Mo host the inclusion of higher angular momenta leads to a smaller, but still significant, reduction of the moments. The calculations are now in good agreement with experiments,

showing that these rather difficult systems are also described well in local density functional theory, provided the numerical calculations are sufficiently accurate.

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