Formation of local spin moments of 3d impurities diluted in noble and alkali metal hosts

1991 J. Phys.: Condens. Matter 3 3777

(http://iopscience.iop.org/0953-8984/3/21/010)

J. Phys.: Condens. Matter 3 (1991) 3777–3784. Printed in the UK

Formation of local spin moments of 3d impurities diluted in noble and alkali metal hosts

N Stefanou and N Papanikolaou
Solid State Section, University of Athens, Panepistimioupolis, New Buildings, GR-157 71, Athens, Greece

Received 14 January 1991

Abstract. We investigate the formation of local spin moments of transition metal impurities diluted in free-electron-like monovalent hosts by performing self-consistent, local spin density functional calculations for all the 3d elements embedded in jellium. The magnetic behaviour of the impurity is studied systematically by varying continuously the jellium density from zero up to a critical value, at which the magnetic moment disappears. Our results are in good agreement with the results of other calculations and the available experimental data.

1. Introduction

The magnetic behaviour of 3d transition metal impurities in sp-band hosts is of continuing experimental [1, 2] and theoretical [3–6] interest. The results obtained from extensive experimental investigations of dilute magnetic 3d sytems are discussed in the light of different models, such as the Friedel-Anderson virtual bound state model [3, 4], Kondo-type models [5], ionic models [6], etc. Moreover, *ab initio* electronic structure calculations [7, 8] have illuminated the problem of the magnetic behaviour of 3d impurities in simple metals.

The variety of host materials has recently been extended to include alkali metals by the pioneering work of Riegel and co-workers [9–11], who applied the time-differential perturbed γ-ray distribution method to investigate the local magnetic behaviour of 3d impurities implanted by recoil into alkali metals.

Study of local moment formation in alkali metals is important because of the wide range of atomic volumes and free electron densities that are accessible. Thus, one can closely study the transition of the 3d-metal impurities from typical solid to atomic configurations which is not possible otherwise. Recently, McHenry *et al* [12] performed self-consistent, local spin density functional calculations of the electronic structure of FeM_{14} and FeM_{26} (M = Li, Na, K, Rb) clusters, modelling an impurity Fe atom in BCC alkali metal hosts. They obtained a local spin-moment of the Fe impurity which grows from $2\mu_B$ (in the Li host) to over $3\mu_B$ (in the Rb host). The calculated crystal field splitting was too small compared with the exchange splitting.

The jellium model, which allows the host electron density to vary continuously, is suitable for the study of the magnetic behaviour of 3d impurities in free-electron-like

0953-8984/91/213777 + 08 $03.50

hosts in a systematic way. This is done in the present article by performing self-consistent calculations within the framework of the density functional theory [13].

2. Calculational method

Self-consistent calculations of the electronic structure of impurities in jellium, based on density functional theory, have been carried out by several authors [14, 15]. In this section we recall the basic assumptions of the jellium model for substitutional impurities and develop the fundamental aspects of our calculational method.

A free-electron-like, monovalent metal of atomic volume

$$\Omega = (4/3)\pi r_s^3 \tag{1}$$

can be likened to a jellium with electron density

$$\bar{\rho} = 3/4\pi r_s^3. \tag{2}$$

The corresponding Fermi level is given by

$$E_F = (9\pi/4)^{2/3}(1/r_s^2). \tag{3}$$

In this paper Rydberg atomic units are used.

The substitutional impurity of atomic number Z_{imp} is embedded in a spherical hole of radius r_s in the positive background. The spherically symmetric perturbing potential is considered to extend up to a distance S around the origin. Within the framework of density functional theory, for a given spherically symmetric total electron density

$$\rho_t(r) = \sum_\sigma \rho_{t,\sigma}(r) \tag{4}$$

where $\rho_{t,\sigma}$ is the electron density for a spin direction σ. The one-electron effective potential is given by

$$V_\sigma(r) = \frac{-2Z_{imp}}{r} + \frac{8\pi}{r}\int_0^r dr'\, r'^2\rho_t(r') + 8\pi\int_r^S dr'\, r'\rho_t(r') + V_{xc,\sigma}[\rho_{t,\sigma}(r)] - V_{xc}(\bar{\rho}) - 4\pi\bar{\rho}(S^2 - r_s^2) \qquad \text{for } r \leqslant r_s \tag{5a}$$

$$V_\sigma(r) = \frac{-2Z_{imp}}{r} + \frac{8\pi}{r}\int_0^r dr'\, r'^2\rho_t(r') + 8\pi\int_r^S dr'\, r'\rho_t(r') + V_{xc,\sigma}[\rho_{t,\sigma}(r)] - V_{xc}(\bar{\rho}) + (4\pi\bar{\rho}/3r) \times (r^3 + 2r_s^3 - 3rS^2) \qquad \text{for } r_s \leqslant r < S \tag{5b}$$

$$V_\sigma(r) = 0 \qquad \text{for } r > S \tag{5c}$$

The term $V_{xc,\sigma}$ describes exchange and correlation effects, which are taken into account through the local spin density approximation of von Barth and Hedin [16] with the parametrization proposed by Moruzzi *et al* [17].

We employ the frozen-core approximation, according to which the core electron density $\rho_c(r)$ is equal to that of an isolated impurity atom. The electron density associated

with the valence states, which extend above an energy E_{inf} and include possible bound states, is calculated from the Green's function

$$\rho_{v,\sigma}(r) = -\frac{1}{\pi}\,\text{Im}\int_{E_{\text{inf}}}^{E_F} \mathrm{d}E\,\Delta G_{v,\sigma}(r, r; E) + \bar{\rho}. \tag{6}$$

ΔG is the difference between the Green's function of the embedded impurity and that of the unperturbed jellium. It is written as

$$\Delta G_{v,\sigma}(r, r; E) = \frac{\sqrt{E}}{4\pi}\sum_{l=0}^{l_{\max}} (2l+1)[R_{l,\sigma}(r; E)H_{l,\sigma}(r; E) - j_l(\sqrt{E}r)h_l(\sqrt{E}r)]. \tag{7}$$

$R_{l,\sigma}$ and $H_{l,\sigma}$ are, respectively, the regular and irregular solutions, of angular momentum quantum number l, of the radial Schrödinger equation for the potential V_σ. Their asymptotic expansions outside the sphere of radius S are given by

$$H_{l,\sigma}(r; E) = h_l(\sqrt{E}r) \tag{8}$$

$$R_{l,\sigma}(r; E) = j_l(\sqrt{E}r) + \sqrt{E}\,t_{l,\sigma}(E)h_l(\sqrt{E}r) \tag{9}$$

where $h_l \equiv y_l - ij_l$. j_l and y_l are the spherical Bessel functions of first and second kind, respectively, [18] and $t_{l,\sigma}$ is the usual scattering t-matrix associated with the potential V_σ. The use of the perturbed Green's function given by (7) allows one to consider a relatively restricted basis in the angular momentum expansions even at large distances r. Indeed, an angular momentum cut-off $l_{\max} = 3$ is usually sufficient to obtain good convergence.

Equations (5), (6) and (7) are solved iteratively using the Tchebycheff iteration scheme [19]. Moreover, the use of the complex energy integration technique [20] accelerates considerably the numerical calculation.

The magnetic moment in Bohr magnetons, μ_B, and the total (positive) charge, within a sphere of radius r around the origin are

$$M(r) = 4\pi\int_0^r \mathrm{d}r'\,r'^2[\rho_{t,\uparrow}(r') - \rho_{t,\downarrow}(r')] \tag{10}$$

$$Q(r) = -4\pi\int_0^r \mathrm{d}r'\,r'^2\rho_t(r') + Z_{\text{imp}} + \Theta(r - r_s)\frac{4\pi}{3}(r^3 - r_s^3) \tag{11}$$

respectively, where $\Theta(r - r_s)$ is the step function.

The total neutrality of the system: jellium + embedded impurity, is described by the Friedel sum rule [3]

$$Z_{\text{imp}} - 1 = \frac{1}{\pi}\sum_\sigma\sum_{l=0}^{l_{\max}}(2l+1)\delta_{l,\sigma}(E_F) \tag{12}$$

where $\delta_{l,\sigma}$ is the scattering phase shift, related to the t-matrix through

$$t_{l,\sigma}(E) = -\frac{1}{\sqrt{E}}\sin\delta_{l,\sigma}(E)\exp[\mathrm{i}\delta_{l,\sigma}(E)] \tag{13}$$

with the boundary condition $\delta_{l,\sigma}(-\infty) = 0$.

3. Results and discussion

We calculated self-consistently the electronic structure of 3d impurities embedded in jellium. For each case we varied the jellium density $\bar{\rho}$ continuously from a dilute limit

corresponding to the Cs host up to the critical value $\bar{\rho}_c$, at which the magnetic moment disappears. Thus, we can closely follow the transition from a magnetic to a non-magnetic state and determine the local spin-moment of the impurity diluted in noble and alkali-metal hosts. Imposing an angular momentum cut-off $l_{max} = 3$ and a range of the perturbing potential $S = 10$ au are sufficient to obtain adequate convergence for the impurity local moment in all cases examined. The total charge enclosed by the sphere $(0, S)$ never exceeds a few hundredths of an electron, and the Friedel sum rule is satisfied to within a few per cent.

Figure 1 shows the local impurity moment within the atomic volume Ω : $M_{loc} \equiv M(r_s)$, for all the 3d elements embedded in jellium, as a function of the jellium density $\bar{\rho}$. The limit $\bar{\rho} = 0$ corresponds to free-atom local density functional calculations [17]. As can be seen from figure 1 the atomic spin-moment cannot be obtained in most cases by smooth extrapolation of the calculated results for the atom embedded in a free-electron gas. This is due to the fact that the distribution of the electron states varies rapidly as the atomic limit is approached. For instance, for a Ni impurity embedded in the most dilute jellium that we considered, the calculated spin-moment comes essentially from the d electrons. The s spin-moment is in this case negligible ($\simeq 0.04\ \mu_B$) but varies rapidly as the atomic limit is approached and finally becomes $1\ \mu_B$ in the case of a free Ni atom.

The formation of a local impurity moment can be understood within the framework of the Anderson model [4]. One can show [21, 22] that an adequate condition for the occurrence of a local moment is

$$In_{loc}(E_F) > 1 \tag{14}$$

where I is the exchange integral. This condition is very similar to Stoner's criterion for elemental ferromagnets, the only difference being that $n_{loc}(E)$ here denotes the paramagnetic local density of states of the impurity and not the host density of states. Thus, favourable conditions for the occurrence of a local moment are a large exchange integral and a high local density of states at E_F. Within the 3d series the condition for magnetism is most likely to apply when the virtual bound state is close to the Fermi energy, since the exchange integral does not vary strongly within the 3d series. Therefore, impurities in the middle of the series, i.e. Cr or Mn, show the strongest tendency to spin polarization and have the largest local moments in a given simple metal host. This is confirmed by our calculations. In a very dense free-electron gas the impurity virtual bound state is so much broadened that the criterion (14) for the formation of a local moment is not 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 3d impurities is shown in figure 2. Cr and Mn become magnetic in a wider range of jellium densities, reflecting their stronger tendency to spin polarization than other transition-metal impurities. In the vicinity of the transition from a spin-polarized to a non-spin-polarized impurity state, the local moment varies as [23]

$$M_{loc} = M_0(1 - \bar{\rho}/\bar{\rho}_c)^{1/2}. \tag{15}$$

This expression is very similar to the result of the Landau theory for second-order phase transitions and also applies for jellium densities far away from the critical point (see figure 1).

Table 1 shows the calculated local moments of 3d impurities diluted in Cu and Ag, together with the results of first-principles calculations by the Korringa-Kohn-Rostoker (KKR) Green's function method [7, 8], which are in good agreement with the available

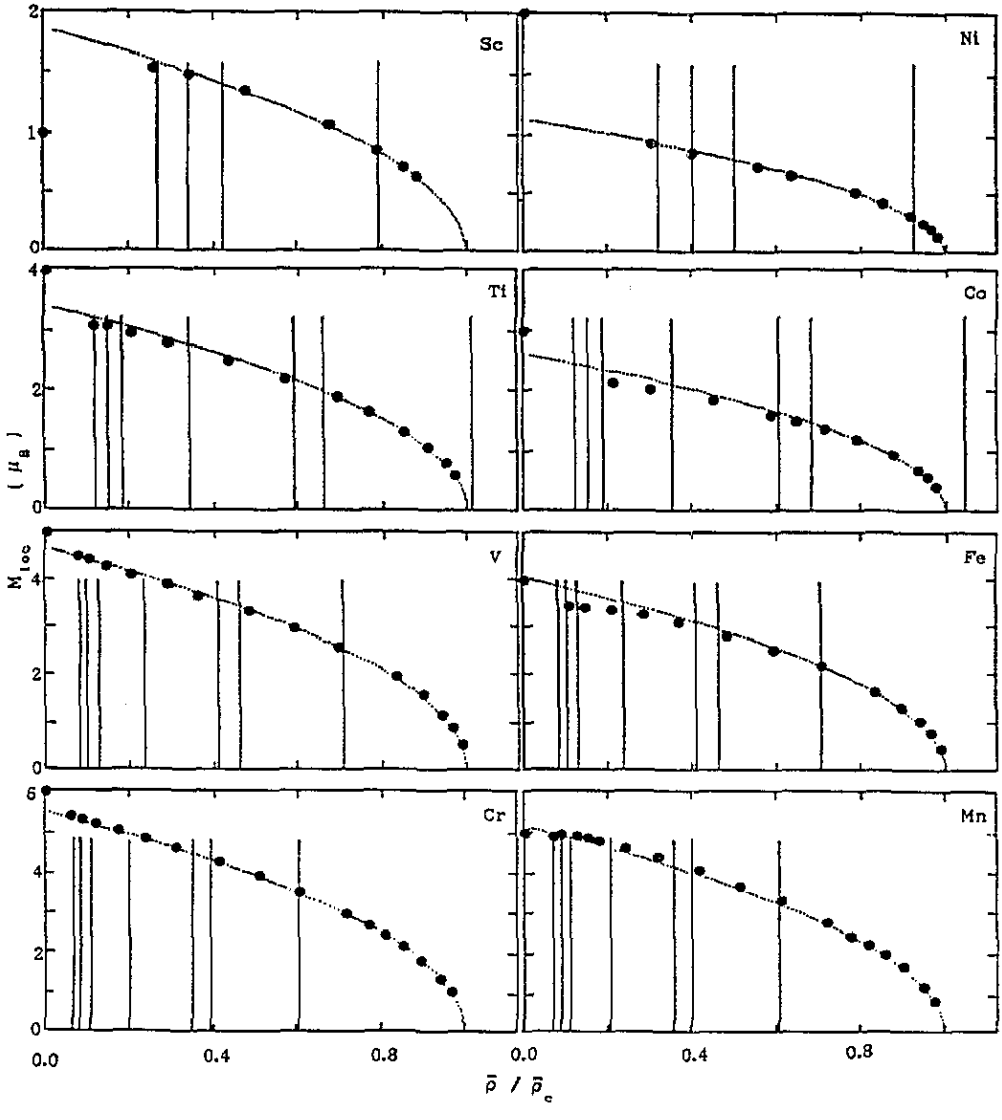

Figure 1. Local moments of 3d impurities in jellium (circles). The dotted curve shows the result of the interpolation formula (15). The vertical lines on the abscissa correspond to the jellium densities of (from left to right): Cs, Rb, K, Na, Li, Ag and Cu. Note that elements with large $\bar{\rho}/\bar{\rho}_c$ are not shown in the figure.

experimental data. The agreement between KKR and jellium results is in general satisfactory. However, as can be seen from table 1, our calculation overestimates the local moment of the early 3d impurities, whereas the moment of the late 3d elements is somewhat underestimated. This can be explained as follows: in a realistic electronic structure calculation the hybridization between the low-lying host 3d and the impurity 3d states repels the impurity d states to higher energies. As a result, for an impurity with a less than half-filled d shell, the local density of states at E_F decreases. This finally leads

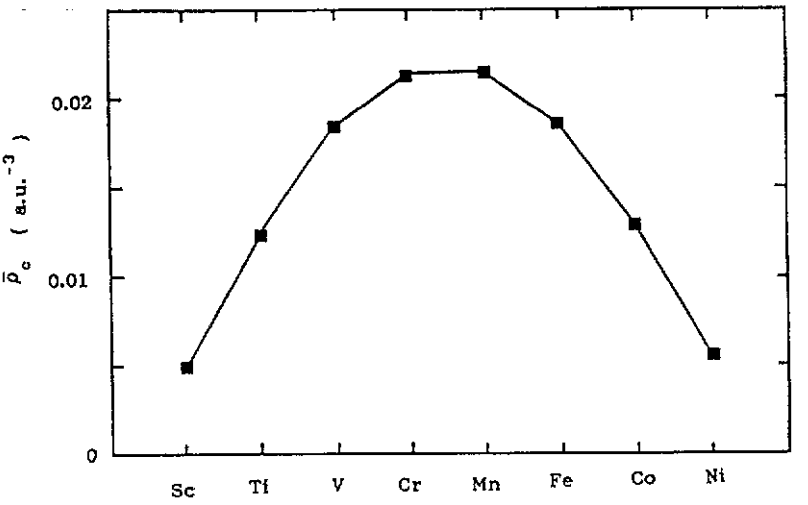

Figure 2. Critical densities of jellium host, $\bar{\rho}_c$, below which each substitutional 3d impurity becomes magnetic.

Table 1. Calculated local moments (in μ_B) of 3d substitutional impurities in Cu and Ag.

	Impurity	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Cu host	Our work	0.00	0.00	2.58	3.52	3.32	2.19	0.00	0.00
	[7]	0.00	0.00	1.44	3.06	3.23	2.30	0.00	0.00
	[8]	0.00	0.00	1.28	3.09	3.44	2.55	0.96	0.00
Ag host	Our work	0.00	1.87	3.33	4.28	4.10	2.85	1.37	0.00
	[7]	0.00	1.35	2.95	4.11	4.06	2.94	1.58	0.00

to a smaller magnetic moment (according to criterion (14)) than obtained in the results of a jellium calculation, where the low-lying host 3d states are neglected. Similarly in our calculation, for an impurity with a more than half-filled d shell, the lack of host d-impurity d hybridization leads to an underestimation of the impurity moment.

In late alkali hosts, the transition metal impurities exhibit an almost atomic behaviour. In the case of Fe impurity, the calculated spin-moment grows from $3\mu_B$ (in the Li host) to $3.5\mu_B$ (in the Cs host). These values are somewhat higher than those calculated by McHenry *et al* [12]. The Fe moment in the largest (27-atom) cluster considered by them grows from $2.12\mu_B$ (in the Li host) to $3.12\mu_B$ (in the Rb host). This slight discrepancy is presumably due to the finite size of the cluster used in their calculations. Our value for the Fe impurity moment in late alkali metal hosts corresponds to a non-integral 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* [9] for the $3d^6$ configuration in spin–orbit coupling with the ground state $J = 4$.

Experimental data are also available for Ni impurities in alkali metals [11]. Our results confirm the experimental finding that Ni in Li is non-magnetic. For Ni in the late

alkali metals: K, Rb and Cs we calculate local moments ranged from $0.82\mu_B$ to $0.92\mu_B$. These values correspond to a non-integral spin ranging from 0.41 to 0.46, in good agreement with the fully localized spin–orbit-coupled $3d^9$ configuration ($S = \frac{1}{2}$, $L = 2$, $J = \frac{5}{2}$) reported from experiment [11]. In the Na host it was found that the magnetic behaviour deviates drastically from that of the pure ionic configuration, and this is consistent with our calculation that yields a local impurity moment of $0.32\mu_B$.

4. Conclusion

We studied the formation of local spin-moments of 3d substitutional impurities in noble and alkali-metal hosts by performing self-consistent, local spin density functional calculations for all the 3d elements embedded in jellium. By continuously varying the jellium electron density we investigated the behaviour of the magnetic moment in the vicinity of the transition from a spin-polarized to a non-spin-polarized solution, without any adjustable parameter.

The calculated impurity moments in noble-metal hosts are in satisfactory agreement with the results of first-principles calculations and experimental data. As we go to lower jellium densities, the host–impurity d hybridization becomes weaker and the magnetic moment increases. In the late alkali-metal hosts the impurities exhibit atomic behaviour and our results are in good agreement with the experimental findings. However, in order to discuss orbital contributions to magnetism, which become important close to the atomic limit, the orbital degeneracy which is inherent in the local spin density approximation used in our calculations, must be removed. This can be achieved by using self-interaction corrections for instance [24].

Acknowledgment

The authors would like to thank Professor P H Dederichs for helpful discussions.

References

[1] Grüner G and Zawadowski A 1974 *Rep. Prog. Phys.* **37** 1497
[2] Grüner G 1974 *Adv. Phys.* **23** 941
[3] Friedel J 1952 *Phil. Mag.* **43** 153; 1954 *Adv. Phys.* **3** 446
[4] Anderson P W 1961 *Phys. Rev.* **124** 41
[5] Kondo J 1969 *Solid State Physics*, vol 23, ed F Seitz, D Turnbull and H Ehrenreich (New York: Academic) p 183
[6] Hirst L L 1970 *Phys. Kondens. Mater.* **11** 255; 1971 *Z. Phys.* **241** 378
[7] Zeller R, Podloucky R and Dederichs P H 1980 *Z. Phys.* B **38** 201
Podloucky R, Zeller R and Dederichs P H 1980 *Phys. Rev.* B **22** 5777
[8] Braspenning P J, Zeller R, Lodder A and Dederichs P H 1984 *Phys. Rev.* B **29** 703
[9] Riegel D, Barth H J, Büermann L, Haas H and Stenzel Ch 1986 *Phys. Rev. Lett.* **57** 388
[10] Riegel D, Büermann L, Gross K D, Luszik-Bhadra M and Mishra S N 1988 *Phys. Rev. Lett.* **61** 2129
[11] Kowallik R, Bertschat H H, Biedermann K, Haas H, Müller W, Spellmeyer B and Zeitz W D 1989 *Phys. Rev. Lett.* **63** 434
[12] McHenry M E, MacLaren J M, Vvedensky D D, Eberhart M E and Prueitt M L 1989 *Phys. Rev.* B **40** 10111
[13] Hohenberg P C and Kohn W 1964 *Phys. Rev.* B **136** 864
Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133

[14] Arponen J, Hautojärvi P, Nieminen R and Pajanne E 1973 *J. Phys. F: Met. Phys.* **3** 2092
Manninen M, Hautojärvi P and Nieminen R 1977 *Solid State Commun.* **23** 795
Nieminen R M and Puska M J 1980 *J. Phys. F: Met. Phys.* **10** L123
Puska M J, Nieminen R M and Manninen M 1981 *Phys. Rev.* B **24** 3037
[15] Stefanou N 1986 *J. Phys. F: Met. Phys.* **16** 837
[16] von Barth U and Hedin L 1972 *J. Phys. C: Solid State Phys.* **5** 1629
[17] Moruzzi V L, Janak J F and Williams A R 1978 *Calculated Electronic Properties of Metals* (New York: Pergamon) p 16
[18] Abramowitz M and Stegun I A 1964 *Handbook of Mathematical Functions* (Washington, DC: Bureau of Standards)
[19] Akai H and Dederichs P H 1985 *J. Phys. C: Solid State Phys.* **18** 2455
[20] Koenig C 1973 *J. Phys. F: Met. Phys.* **3** 1497
Dreysse H and Riedinger R 1982 *J. Physique* **42** 437
Zeller R, Deutz J and Dederichs P H 1982 *Solid State Commun.* **44** 993
[21] Mott N F 1974 *Metal–Insulator Transitions* (London: Taylor and Francis) p 94
[22] Dederichs P H, Akai H, Blügel S, Stefanou N and Zeller R 1989 *Alloy Phase Stability NATO ASI* ed G M Stocks and A Gonis (Deventer: Kluwer) p 377
[23] Stefanou N 1986 *PhD Thesis* Université de Strasbourg I
Stefanou N, Zeller R and Dederichs P H 1987 *Phys. Rev.* B **35** 2705
Stefanou N, Braspenning P J, Zeller R and Dederichs P H 1987 *Phys. Rev.* B **36** 6372
[24] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048