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The hyperfine field at rare-earth impurities diluted in Fe, Co and Ni hosts: a theoretical study

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Abstract

In this work we study the magnetic moments and the hyperfine fields at rare-earth impurities diluted in Fe, Co and Ni ferromagnetic hosts. We use an Anderson-like model in which a degenerate localized 4f energy level of the rare-earth impurity is hybridized with a spin-polarized d-electron band. We use the Hartree–Fock approximation to deal with the electron–electron interactions and include the nearest-neighbour perturbation, due to the d translational invariance breaking introduced by the impurity. Our numerical results show that the systematics of the hyperfine fields changes sign in the middle of the rare-earth series and exhibits a strong orbital contribution for most of the rare-earth impurities, in good agreement with experimental data.

1. Introduction

The formation of local moments and its connection to the hyperfine interactions is one of the central problems in the description of the magnetic properties of metals [1–7]. In particular, many theoretical works based either on first-principles calculations or on model approaches have been devoted to the study of the systematics of the magnetic moments and the hyperfine fields at impurity sites diluted in ferromagnetic transition metals and rare-earth hosts [7–22]. Very recently, we have extended a theoretical formulation including the change in the energy of the hopping between the impurity and the nearest neighbours [23–25] to study the local magnetic moments and the hyperfine fields at La, Gd and Lu impurities diluted in Fe and Ni ferromagnetic hosts [22]. In that work we did not take into account the orbital contribution to the total magnetic moment, since La, Gd and Lu exhibit $4f^0$, $4f^7$ and $4f^{14}$ electronic configurations respectively. However, most of the rare-earth impurities develop large electronic magnetic moments, composed of both spin and orbital contributions. The hyperfine interactions of the rare-earth impurities are in general strong, and dominated by orbital effects, as indicated by the available experimental data [26]. Therefore it is very important to consider the spin and the orbital magnetic moments in the theoretical calculation of the hyperfine fields of the rare-earth impurities diluted in the metallic hosts.

On the basis of the above considerations, in this paper we study theoretically the local magnetic moments and the hyperfine fields of the rare-earth impurities diluted in Fe, Co and Ni hosts. For this purpose, we use an extended Anderson model Hamiltonian [2,3], in which the 4f energy level of the rare-earth impurity is coupled to a host exchange-polarized d band perturbed by a local charge- and spin-dependent potential. In the framework of this model, which is very similar to the one used by Coqblin and Blandin to discuss the stability of localized magnetic moments in metals [27], the hybridization between the charge-perturbed ferromagnetic d band and the localized 4f energy level plays an important role in the formation of the local magnetic moments of the rare-earth impurities. Our numerical results show that the systematics of the hyperfine fields changes sign in the middle of the rare-earth series and has also a strong orbital contribution for most of the rare-earth impurities, in good agreement with experimental data.

2. Theoretical model

In order to describe the magnetic moments and the hyperfine fields at rare-earth impurities diluted in a ferromagnetic transition metal host, we start with the following Hamiltonian:

$$H = H_0 + V^d + V^f + V^{df} \tag{1}$$

where

$$H_0 = \sum_{j,\sigma} \varepsilon_h^d d_{j\sigma}^\dagger d_{j\sigma} + \sum_{j,l,\sigma} t_{jl\sigma}^{dd} d_{j\sigma}^\dagger d_{l\sigma} + \sum_j U_h^d n_{j\uparrow}^d n_{j\downarrow}^d \tag{2}$$

$$V^d = (\varepsilon_I^d - \varepsilon_h^d) + (U_I^d - U_h^d) n_{0\uparrow}^d n_{0\downarrow}^d + \tau_d \sum_{j\neq 0,\sigma} t_{0j}^d (d_{0\sigma}^\dagger d_{j\sigma} + d_{j\sigma}^\dagger d_{0\sigma}) \tag{3}$$

$$V^f = \sum_{m,\sigma} \varepsilon_0^f f_{0m\sigma}^\dagger f_{0m\sigma} + \tfrac{1}{2} \sum_{m,m',\sigma} U_{mm'}^f n_{m\sigma}^f n_{m'-\sigma}^f + \tfrac{1}{2} \sum_{\substack{m,m',\sigma \\ (m\neq m')}} (\bar{U}_{mm'}^f - J_{mm'}^f) n_{m\sigma}^f n_{m'\sigma}^f \tag{4}$$

$$V^{df} = V_0^{df} \sum_{m,\sigma} (d_{0\sigma}^\dagger f_{0m\sigma} + f_{0m\sigma}^\dagger d_{0j\sigma}). \tag{5}$$

Here H_0 is the Hamiltonian for the pure ferromagnetic host and V^d is a non-local impurity potential. τ_d is an impurity-dependent parameter which renormalizes the energy hopping between impurity and host sites with respect to the energy hopping between one host site and another. V^f describes the degenerate 4f energy level of the rare-earth impurity, where m and m' denote the 4f-orbital levels. V^{df} describes the coupling between the degenerate 4f energy level and the d energy band, where V_0^{df} is a parameter of the model. ε_I^d and ε_0^f are energy levels of the impurity state; ε_h^d is the host d-energy-band centre and $t_{jl\sigma}^{dd}$ is the d-electron energy hopping. $d_{j\sigma}^\dagger$ ($d_{j\sigma}$) is the creation (annihilation) operator for d electrons at site j with spin σ in the Wannier representation; $f_{0\sigma}^\dagger$ ($f_{0\sigma}$) is the creation (annihilation) operator for f electrons at the impurity site. U_h^d (U_I^d) is the d–d Coulomb correlation parameter at the host (impurity) site, $U_{mm'}^f$ is the usual Coulomb correlation between f electrons, whereas $\bar{U}_{mm'}^f$ and $J_{mm'}^f$ ($m \neq m'$) are the interband f–f Coulomb and exchange correlations respectively.

In order to deal with the above Hamiltonian, we proceed as follows. In a first step we disregard the 4f energy level and consider only the charge and spin perturbation due to the 5d states of the impurity, i.e., one has a Wolff–Clogston impurity problem [4, 5]. In the Hartree–Fock approximation, the perturbed Green function for the Hamiltonian (1), without the terms V^f and V^{df}, is given by

$$\tilde{g}_{00\sigma}^{dd}(z) = \frac{g_{00\sigma}^{dd}(z)}{\alpha_d^2 - g_{00\sigma}^{dd}(z)[(\alpha_d^2 - 1)(z - \varepsilon_{h\sigma}^d) + V_{0\sigma}^d]} \tag{6}$$

where $g^{dd}_{00\sigma}(z)$ is the host Green function; $z = \varepsilon + \mathrm{i}0$; $\alpha_d = \tau_d + 1$ and $\varepsilon^d_{h\sigma} = \varepsilon^d_h + U^d_h\langle n^d_{-\sigma}\rangle$. The local potential $V^d_{0\sigma}$ is given by

$$V^d_{0\sigma} = \Delta\varepsilon^d + (U^d_I - U^d_h)\langle n^d_{-\sigma}\rangle + U^d_I\delta\langle n^d_{0-\sigma}\rangle \tag{7}$$

where $\Delta\varepsilon^d = \varepsilon^d_I - \varepsilon^d_h$ and $\delta\langle n^d_{0-\sigma}\rangle = (\langle n^d_{-\sigma}\rangle - \langle n^d_{0-\sigma}\rangle)$. Following the usual procedure [21], the change in the d-electron occupation number per spin state is given by

$$\Delta Z^d_\sigma = -\frac{1}{\pi}\,\mathrm{Im}\ln\{\alpha^2_d - g^{dd}_{00\sigma}(\epsilon_F)[(\alpha^2_d - 1)(\epsilon_F - \varepsilon^d_{h\sigma}) + V^d_{0\sigma}]\} \tag{8}$$

where ϵ_F is the Fermi energy. The local potential $V^d_{0\sigma}$ is self-consistently determined using the Friedel screening condition for the total charge difference ΔZ^d, i.e., $\Delta Z^d = \Delta Z^d_\uparrow + \Delta Z^d_\downarrow$.

In the second step of our approach, we consider the degenerate localized 4f energy level of the rare-earth impurity to be coupled to a local perturbed d density of states, obtained by taking the imaginary part of the perturbed Green function $\tilde{g}^{dd}_{00\sigma}(z)$ for the impurity problem in the Wolff–Clogston picture. Therefore, one has an Anderson–Moriya [2, 3] impurity embedded in a Koster–Slater [28] perturbed conduction electron gas. In this approach the local Green functions for d electrons, $G^{dd}_{00m\sigma}(z)$, and for f electrons, $G^{ff}_{00m}(z)$, at the impurity site are given by

$$G^{dd}_{00m\sigma}(z) = \tilde{g}^{dd}_{00\sigma}(z) + \tilde{g}^{dd}_{00\sigma}(z)g^{ff}_{00\sigma}(z)|V^{df}_0|^2 G^{dd}_{00m\sigma}(z) \tag{9}$$

$$G^{ff}_{00m\sigma}(z) = g^{ff}_{00\sigma}(z) + g^{ff}_{00\sigma}(z)|V^{df}_0|^2\tilde{g}^{dd}_{00\sigma}(z)G^{ff}_{00m\sigma}(z) \tag{10}$$

where $g^{ff}_{00m\sigma}(z) = [z - \varepsilon^f_{m\sigma}]^{-1}$ is the non-hybridized local f Green function. After simple algebra we obtain the local Green functions at the impurity site as

$$G^{dd}_{00m\sigma}(z) = \frac{(z - \varepsilon^f_{m\sigma})\tilde{g}^{dd}_{00\sigma}(z)}{z - \varepsilon^f_{m\sigma} - |V^{df}_0|^2\tilde{g}^{dd}_{00\sigma}(z)} \tag{11}$$

$$G^{ff}_{00m\sigma}(z) = \frac{1}{z - \varepsilon^f_{m\sigma} - |V^{df}_0|^2\tilde{g}^{dd}_{00\sigma}(z)} \tag{12}$$

where the renormalized energy level $\varepsilon^f_{m\sigma}$ is given in the Hartree–Fock approximation by

$$\varepsilon^f_{m\sigma} = \varepsilon^f_0 + \sum_{m'} U^f_{mm'}\langle n^f_{m'-\sigma}\rangle + \sum_{m'\neq m}\tilde{U}^f_{mm'}\langle n^f_{m'\sigma}\rangle \tag{13}$$

where $\tilde{U}^f_{mm'} = (\bar{U}^f_{mm'} - J^f_{mm'})$. The hybridized 5d and 4f densities of states at the rare-earth impurity site are calculated by taking the imaginary parts of the local Green functions $G^{dd}_{00m\sigma}(z)$ and $G^{ff}_{00m\sigma}(z)$ respectively, i.e., $\tilde{\rho}^d_{0m\sigma}(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,G^{dd}_{00m\sigma}(z)$; $\tilde{\rho}^f_{0m\sigma}(\varepsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,G^{ff}_{00m\sigma}(z)$. The 5d- and 4f-electron occupation numbers at the impurity site are calculated by integrating the corresponding local densities of states up to the Fermi Level, i.e., $\tilde{n}^d_{0m\sigma} = \int_{-\infty}^{\epsilon_F}\tilde{\rho}^d_{0m\sigma}(\varepsilon)\,\mathrm{d}\varepsilon$; $\tilde{n}^f_{0m\sigma} = \int_{-\infty}^{\epsilon_F}\tilde{\rho}^f_{0m\sigma}(\varepsilon)\,\mathrm{d}\varepsilon$. For a given hybridization parameter V^{df}_0, the energy level ε^f_0 is obtained self-consistently using the condition for the total occupation number at the impurity site, i.e., $\tilde{n}_{0\sigma} = \sum_m(\tilde{n}^d_{0m\sigma} + \tilde{n}^f_{0m\sigma})$. The 5d magnetic moment at the impurity site is calculated from $\tilde{m}_d(0) = \sum_m(\tilde{n}^d_{0m\uparrow} - \tilde{n}^d_{0m\downarrow})$. The total f magnetic moment at the impurity site is given by $\tilde{m}_f(0) = \tilde{m}^{spin}_f(0) + \tilde{m}^{orb}_f(0)$, where $\tilde{m}^{spin}_f(0) = \sum_m(\tilde{n}^f_{0m\uparrow} - \tilde{n}^f_{0m\downarrow})$ and $\tilde{m}^{orb}_f(0) = \sum_m m(\tilde{n}^f_{0m\uparrow} + \tilde{n}^f_{0m\downarrow})$ are respectively the spin and the orbital contributions.

Once the magnetic moments are self-consistently determined, the total magnetic hyperfine field B^{tot}_{hf} at the rare-earth impurity site is given by

$$B^{tot}_{hf} = B^c_{hf} + B^d_{hf} + B^f_{hf} = A(Z_{imp})\tilde{m}_c(0) + A^{5d}_{cp}\tilde{m}_d(0) + A^{4f}_{cp}\tilde{m}_f(0). \tag{14}$$

Here for the sake of numerical simplicity we take the s–p magnetic moment at the impurity site $\tilde{m}_c(0)$ as proportional to the d host magnetization [29], i.e., $\tilde{m}_c(0) = -\gamma m_d$, with the proportionality constant γ of the order of 0.1. A_{cp}^{5d} and A_{cp}^{4f} are the 5d and 4f core polarization coupling parameters respectively [8, 14, 30]. Here we take $A_{cp}^{5d} = -100$ T/μ_B and $A_{cp}^{4f} = -150$ T/μ_B [8,13,30]. The impurity-dependent Fermi Segrè coupling parameters $A(Z_{imp})$ were obtained from the following linear interpolation expression:

$$A(Z_{imp}) = A(Z_{La}) + \frac{[A(Z_{Lu}) - A(Z_{La})]}{14}(Z_{imp} - Z_{La}) \tag{15}$$

where Z_{imp} is the atomic number of the impurity; $A(Z_{La}) = 310$ T/μ_B and $A(Z_{Lu}) = 480$ T/μ_B [8].

3. Numerical results and discussion

First we consider the case of the rare-earth impurities diluted in an Fe host. We adopted a model 3d density of states extracted from first-principles calculations, like in [21]. The host Coulomb interaction parameter ($U_h^d = 0.6$) was chosen to adjust correctly the experimental value of the magnetic moment of the iron host, i.e., $m_d(\mathrm{Fe}) = 2.2\ \mu_B$. For the impurity, we adopted the parameter α_d (which renormalizes the energy hopping involving the impurity site with respect to the energy hopping involving only host sites) as 1.35 for all rare-earth impurities. This choice in consistent with the ratio between the extents of the 5d and the 3d atomic wavefunctions of the rare-earth impurity and the host atoms respectively. The impurity d–d Coulomb interaction parameter was chosen to be smaller than the host one. Here we used $U_I^d = 0.5U_h^d$. These Coulomb parameters are also consistent with the extents of the 3d and 5d atomic wavefunctions. With these parameters, we calculated the perturbed density of states at the rare-earth impurity site.

The parameter describing the hybridization between the 4f energy level and the perturbed d density of states was taken as $|V_0^{df}|^2 = 0.04$, in units of the width of the Fe 3d band. We considered the parameter $U_{mm'}^f$, describing the Coulomb interaction between f electrons with opposite spins, to be independent of the f-orbital label, i.e., $U_{mm'}^f = U_{mm}^f = U^f$, and we adopted for this parameter $U^f = 2.0U_h^d$. We considered the interband parameter $\tilde{U}_{mm'}$ which accounts for the appearance of the f-orbital magnetic moments as being $\tilde{U}_{mm'} = \tilde{U}_{mm} = \tilde{U}_m$. In the cases of La, Gd and Lu, since no orbital contribution is expected, we made the further approximation $\tilde{U}_m = \tilde{U}_0$ (i.e., independent of the m-orbital level), and we adopted the value $\tilde{U}_0 = 0.9U^f$. For the other rare-earth impurities, the existence of the orbital contribution is due to there being a set of parameters $\tilde{U}_m$, all different. In our calculations, we considered $\tilde{U}_m$ ($|m| = 0, 1, 2, 3$), assuming values with small variations about $\tilde{U}_0$.

With these parameters, we self-consistently obtained the hybridized 5d and 4f densities of states at the impurity sites and calculated the corresponding local magnetic moments. In figure 1(a) we show the calculated spin parts of the 5d and 4f magnetic moments at the rare-earth impurity site. The spin 5d and 4f magnetic moments are very small, compared to the 4f-orbital contribution. In figure 1(b) we plot the 4f-orbital contribution to the total magnetic moment at the rare-earth impurity site in Fe host (solid line). From this figure, we can observe that the systematics of the orbital contribution to the total magnetic moment is dominant for most of the rare-earth impurities and changes sign in the middle of the series (in the case of Gd, where $L = 0$). Accordingly, the calculated hyperfine fields at the rare-earth impurities diluted in the Fe host, shown by the solid line of figure 2(a), have mainly orbital character and exhibit a change of sign in the middle of the series, in good agreement with experimental data [26].

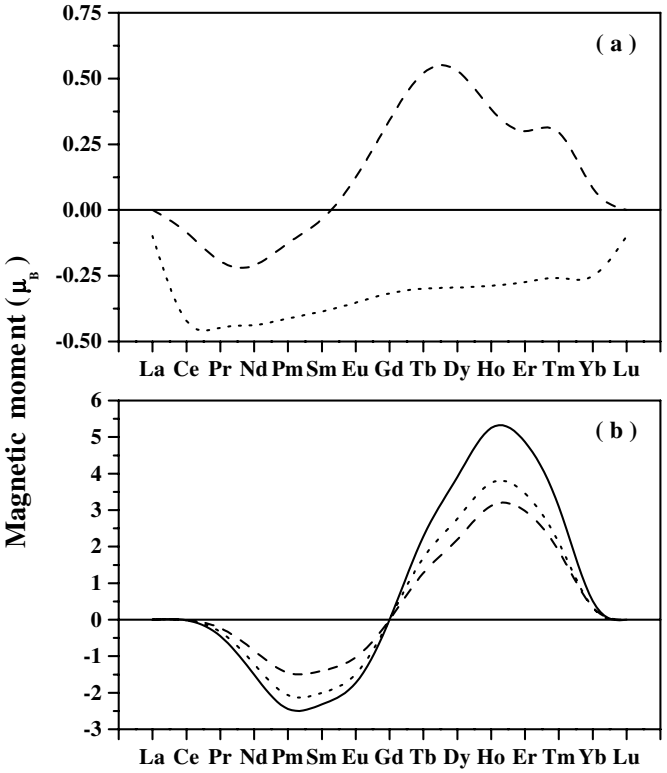

Figure 1. (*a*) Contributions to the local magnetic moments at the rare-earth impurities diluted in an Fe host. The dotted curve represents the spin part of the 5d magnetic moments, whereas the dashed curve corresponds to the spin part of the 4f magnetic moments. In (*b*) we plot the local 4f-orbital magnetic moments at the rare-earth impurities diluted in Fe (solid curve), Co (dotted curve) and Ni (dashed curve) hosts.

Now we consider the systematics of the magnetic moments and the hyperfine fields of the rare-earth impurities diluted in Co and Ni hosts. In order to describe Co and Ni hosts, we adopted 3d densities of states parametrized from first-principles calculations [31]. The 3d Coulomb interaction parameters were chosen to adjust correctly the experimental magnetic moments of 1.7 and 0.6 μ_B of the Co and Ni hosts: $U_h^d(\mathrm{Co}) = 0.7$ and $U_h^d(\mathrm{Ni}) = 0.9$, respectively. As regards the rare-earth impurity parameters, they are the same as those used in the previous case of the Fe host, except for the effective hybridization parameters, taken here, in units of the width of the Fe 3d band, as $|V_0^{df}|^2 = 0.075$ for the case of the Co host and $|V_0^{df}|^2 = 0.085$ for the case of the Ni host. Following the same procedure as was used for the case of the Fe host, we self-consistently calculated the magnetic moments and the hyperfine fields at the rare-earth impurity sites. In figure 1(*b*) we plotted the 4f-orbital magnetic moments at the rare-earth impurity site in Co (dotted curve) and Ni (dashed curve) hosts.

The systematics of the calculated hyperfine fields for the rare-earth impurities diluted in a Ni host (dashed curve of figure 2(*a*)) describe quite well the available experimental data [26,32]. In the case of a Co host (dotted curve of figure 2(*b*)), there are discrepancies between our theoretical results and experimental data (e.g., for Nd**Co** and Sm**Co**). This is because the experiments where performed at $T = 320$ and 300 K for Nd**Co** and Sm**Co** respectively, whereas our calculations were performed at $T = 0$ K. It is known that the conduction electron

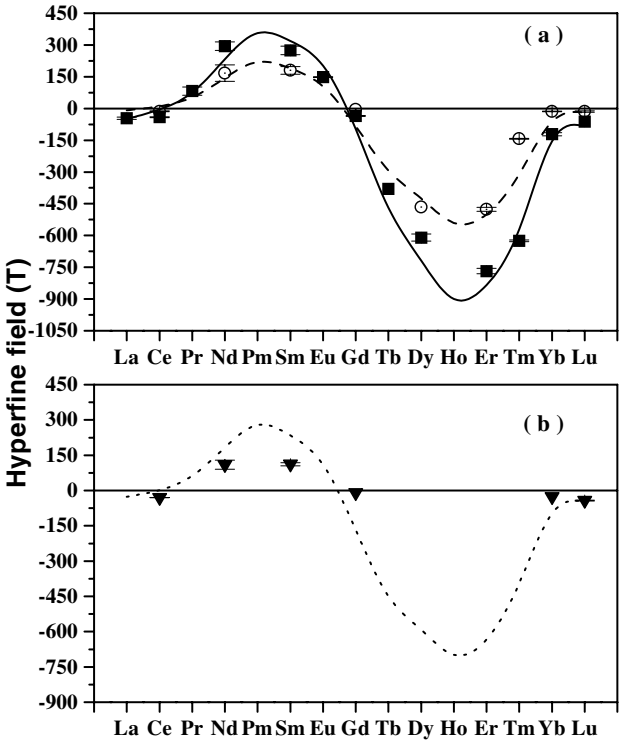

Figure 2. Systematics of the hyperfine fields at the rare-earth impurities diluted in Fe, Ni hosts (*a*) and a Co host (*b*). The solid and dashed curves correspond to the theoretical calculation for the Fe and Ni hosts respectively. The dotted curve corresponds to the theoretical calculation for the Co host. The experimental data for Fe (squares), Ni (circles) and Co (triangles) hosts have been collected from [26, 32].

polarization contribution to the magnetic hyperfine field is not affected by temperature, whereas the 'accidents' of the d band as well as the f hump (originating from the d–f hybridization of the f level and the d band) are strongly affected by temperature [13, 22]. So, one expects a decrease in the core polarization contribution to the hyperfine field, and therefore the total hyperfine fields would decrease also in accordance with the available experimental results.

In conclusion, in this paper we have discussed the systematics of the magnetic moments and the hyperfine fields at rare-earth impurities diluted in the Fe, Co and Ni ferromagnetic hosts. The results obtained show that for most of the rare-earth impurities, the hyperfine fields exhibit a change of sign in the middle of the rare-earth series and have a strong orbital contribution, in good agreement with the experimental data. It is worth mentioning here that the case of actinide impurities diluted in a ferromagnetic host can be addressed using the model presented in this paper. Calculations in this direction are now in progress [33].

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