HYPERFINE FIELDS AND LOCAL MOMENT FORMATION AT IMPURITIES IN Gd METAL

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ABSTRACT

Firstly, we discuss, an extension of the Daniel-Friedel model, to describe the hyperfine field at a non-magnetic (noble or s–p) impurity in Gd. It is found, that our model can qualitatively explain the measured hyperfine fields at these impurities.

We discuss also the hyperfine fields at d-transition impurities in Gd employing a two-band s-d model in an extended RKKY picture. The observed general trends of the measured hyperfine fields is well reproduced by our calculation.

Finally, an intermediate valence model for anomalous rare earth impurities such as Ce, Sm, Eu and Yb in Gd is used to describe the formation of the local moments. These impurities are described as strongly d-f correlated and hybridized systems and the valence of these impurities are obtained. Agreement with both theoretical claims and experimental results is obtained.

1. INTRODUCTION

In a series of papers published in recent years[1-4], we have discussed the hyperfine fields of s-p, noble and transition impurities in ferromagnetic Gadolinium. These studies have been based on very simple models which describe quite well the general trend of the available hyperfine field measurements. We summarize in this paper our discussion on the local moment formation or retention (i.e., local magnetization) at the impurity sites, which are closely related to the theoretical analysis of the hyperfine field data in these dilute alloys. We also extend our study to discuss the hyperfine field at "anomalous" rare earth impurities such as Ce, Sm, Eu and Yb placed in Gd metal.

In the following Section (Sect. 2) we present the adopted model to describe the ferromagnetic Gd host. In Sect. 3 we discuss the model which accounts for the hyperfine field data at s-p and noble impurities, whereas Sect. 4 is devoted to discuss the case of transition impurities.

In Sect. 5 we discuss the "anomalous" rare earth impurities and we make also supplementary discussions.

2. DESCRIPTION OF THE FERROMAGNETIC HOST

It seems now well established that Gd, the only heavy rare earth which goes directly from a paramagnetic to a ferromagnetic state (T_c = 292.2K) without passing through an oscillatory or helical structure, is a normal ferromagnetic metal with a complex temperature dependence of the direction of the host magnetic moment, which is however mostly irrelevant to the discussions here presented and will thereby here be disregarded.

Band calculations[5,6] have shown that Gd metal exhibits d-bands contributing a high density of states in the vicinity of the Fermi energy E_F, and in this sense can be considered as a transition-like metal in the beginning of a 5d-series. Ferromagnetic Gd metal differs from 3d-ferromagnetics in some aspects. For instance, in Gd, the localized 4f-moment contributes 7.0 Bohr magnetons to the total magnetization. The conduction band, which is both of d-character (mostly) and of s-p character contributes about 0.63 Bohr magnetons[7]. In the present calculation the d-band and s-p band occupations numbers are taken as being respectively $< n_d > = 2.2$ electrons (per host atom) and $< n_c > = 0.8$ electrons (per host atom), giving a Gd^{3+} configuration ($< n_d > + < n_c > = 3.0$), as estimated in[8].

The ferromagnetism of Gd host metal is described here in a simple Stoner-like picture by two d-character spins subbands generated by an average exchange energy splitting. The splitting ϵ_d between up and down spin subbands is given by

$$\epsilon_d = -2J_{df} < S_z > - U\,(< n_{d\sigma} > - < n_{d-\sigma} >), \qquad (1)$$

where J_{df} is the exchange interaction between f-moments and d-conduction electrons, $< S_z >$ is the Gd 4f-spin and U is the d-d Coulomb type interaction. The number of d-electrons with spin up and spin down, $< n_{d\sigma} >$ and $< n_{d-\sigma} >$, satisfay the equations

$$< n_{d\sigma} > - < n_{d-\sigma} > = m_d, \qquad (2)$$

$$< n_{d\sigma} > + < n_{d-\sigma} > = < n_d >, \qquad (3)$$

where m_d is the d-magnetization of the host.

The polarized s-p conduction band is considered to be made up of four identical s-p subbands (per spin

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direction). Assuming that s-p and d-band have antiparallel magnetizations (as in the case of Fe)[9], one has:

$$m_c = \langle n_{c\sigma} \rangle - \langle n_{c-\sigma} \rangle = -\alpha_{cd} m_d \,, \qquad (4)$$

where α_{cd} is a phenomenological parameter, whose of magnitude, estimated from the study of transition metals, is $\alpha_{cd} \approx 0.1$.[9] One has also:

$$\langle n_{c\sigma} \rangle + \langle n_{c-\sigma} \rangle = n_c \,. \qquad (5)$$

Note that assumption (4) leads to a negatively uniformly s-p conduction band, in contrast with Campbell's calculation for the Gd host case[10], which is a positively one. Moreover, although Campbell's approach seems to consider Fe and Gd as being hosts which exhibit essentially the same nature as far as their ferromagnetic character is concerned, i.e., a twofold split d-character subbands with opposite spins, both of them partially filled, in the Gd case, the d-electrons have been completely ignored in that calculation[10].

3. LOCAL MOMENTS OF s-p AND NOBLE IMPURITIES IN Gd

Magnetic Hyperfine Field measurements at non-magnetic elements placed in ferromagnetic Gd metal are directly related to the charge and spin dependent locally perturbed density-of-states $\tilde{\rho}_0$ (e) and therefore they provide unique information on the local moment formation (or local magnetization) at these sites.

The sistematic behaviour of magnetic hyperfine fields (H_{hf}) at non-magnetic s-p impurities, substitutionally dissolved in pure ferromagnetic 3d-hosts such as Fe, Co, and Ni, has been extensively studied in the past two decades. It has been shown experimentally that the hyperfine fields are sistematically negative in the first that of s-p series and positive for s-p elements in the second half, a crossover ocurring near the middle of the s-p series[11].

According to the work of Daniel and Friedel[12], the above mentioned change in sign of the hyperfine field is believed to be mostly a conduction electron effect. There have been many theoretical improvements based on the Daniel-Friedel (DF) local potential model in order to explain such observed hyperfine field systematics[13,14]. In particular, Campbell[13] developed a calculation, within a tight-binding approach, closely related to the DF model, but ascribing to s-d host hybridization a fundamental role. This leads to a negative magnetization m_c of the s-p host conducting band and the model is quite successful in explaining the negative field observed for Ag, Cd, In, and Sn impurities embedded in Fe.

The magnetic hyperfine interaction for non-magnetic (s-p and noble) impurities in ferromagnetic rare earth metals has been much less studied than for ferromagnetic 3d-metals. In the case of Gd host there are systematic data concerning hyperfine fields at 4sp-and 5sp- nuclei. The sign of the fields at the s-p and noble site is always negative and no change in sign is observed when one goes along a s-p series[11,15].

In this section we suggest a mechanism based on Campbell's aproach[13] to the DF model, which considers both d- and s-p host conduction electrons and accounts for the peculiarities of metallic Gd host.

The 4f-Gd spins polarize the d-conduction band which acts as an effective external magnetic field on the host s-p conduction band. As mentioned is Sect. 1, one assumes that, due to host s-d hybridization, the s-p and d-conduction bands have antiparallel magnetizations, as occurs in Fe metal[9]. The polarized s-p conduction band is considered to be made up of four identical s-p subbands (per spin direction), which are properly orthogonalized with respect to the other inner core states.

The s-p electrons are acted on by charge and spin dependent localized DF-type potentials V_σ at the impurity site. The overall change in the number of states introduced by such potential for electrons with spin σ is (Friedel's sume rule[16]):

$$\Delta Z_\sigma (V_\sigma) = -\frac{4}{\pi} \operatorname{arctg} \frac{\pi V_\sigma \rho_\sigma (E_F)}{1 - V_\sigma F_\sigma (E_F)} \,, \qquad (6)$$

where ρ_σ (E) is the s-p conduction host density of states corresponding to a σ-subband, F_σ (E) is its Hilbert transform and E_F is the Fermi energy.

The number of s-p electrons per spin σ at the impurity site is:

$$\tilde{n}_\sigma (0;\lambda) = \int_{E_b}^{E_F} \tilde{\rho}_\sigma (E;\lambda)\, dE + \frac{F_\sigma^2 (E_{0\sigma})}{\left| \frac{dF_\sigma (E_{0\sigma})}{dE} \right|} =$$

$$= \int_{E_b}^{E_F} \frac{\rho_\sigma (E)\, dE}{[1 - V_\sigma F_\sigma (E)]^2 + [\pi V_\sigma \rho_\sigma (E)]^2} +$$

$$+ \frac{F_\sigma^2 (E_{0\sigma})}{\left| \frac{dF_\sigma (E_{0\sigma})}{dE} \right|} \,, \qquad (7)$$

where E_b is the bottom of the s-p conduction subband with spin σ. $\tilde{n}_\sigma (0;\lambda)$ involves: (i) the contribution arising from the continuous spectrum through the amplitude at the impurity site of the occupied Slater-Koster (SK) perturbed states $\tilde{\rho}_\sigma (E;\lambda)$ and (ii) the amplitude at the impurity site of the bound state (if eventually present and occupied), the pole $E_{0\sigma}$ being defined by:

$$1 - V_\sigma F_\sigma (E_{0\sigma}) = 0.$$

The localized potential at the non-magnetic impurity site is given by:

$$V_\sigma = V_0 - \sigma\epsilon_0 = V_0 - \sigma\lambda\epsilon_c \,, \qquad (8)$$

where V_0 is a purely electrostatic perturbation arising from the difference of charge ΔZ between the non magnetic impurity and s-p host conduction electrons:

$$\Delta Z = Z_{imp} - Z_{host}^{sp} = \sum_\sigma \Delta Z_\sigma (V_\sigma) \,, \qquad (9)$$

and the potentials V_σ satisfy the DF condition:

$$V\downarrow - V\uparrow = 2\epsilon_0 = 2\lambda\epsilon_c \,. \qquad (10)$$

ϵ_0 is the net spin splitting at the impurity site, whereas ϵ_c is the exchange s-p subband splitting which is proportional to the host d-magnetization. One has $\epsilon_0 \neq \epsilon_c$, the factor λ $(0 < \lambda < 1)$ being a phenomenological parameter which accounts for the transferred magnetization of Ruderman-Kittel-Kasuya-Yosida (RKKY) type, created by the ordering of the Gd 4f-electrons.

So, a new parameter $\lambda = \epsilon_0/\epsilon_c$, with respect to the standard DF-type models, is introduced, which is of crucial importance in the discussion of the self-consistent local magnetization at the impurity site. This parameter, is in some sense a measure of the transferred magnetization via RKKY. In the case of 3d-ferromagnetic hosts $\epsilon_0 \simeq \epsilon_c$, and one has $\lambda \simeq 1$, thus recovering the usual DF model.

In the present numerical calculation, we have taken parabolic bands described by

$$\rho(E) = \frac{3}{4W} \left[1 - \left(\frac{E}{W} \right)^2 \right], \tag{11}$$

W being the conduction bandwidth. With that choice, F(E) turns out to be

$$F(E) = \frac{3}{4W^3} \left[2EW + (W^2 - E^2) \ln \frac{E+W}{E-W} \right]. \tag{12}$$

From equation (2) one obtained the local magnetization:

$$\tilde{m}(0;\lambda) = \sum_{\sigma} \sigma \tilde{n}_{\sigma}(0;\lambda), \tag{13}$$

and the conduction electron polarization (CEP) hyperfine field is given by:

$$H_{hf} = A(z)\tilde{m}(0;\lambda), \tag{14}$$

where A(Z) is the Fermi-Segrè hyperfine contact parameter, as estimated by Campbell[13].

Equation (7) shows that only integrations over the density of states are needed. So, one may hope that the form of ρ (E) is not critical, and a model density of states like equation (11) is suitable.

The self-consistent numerical calculations for the s-p impurities are shown in Fig. 1. For the sake of comparison we have plotted the experimental hyperfine fields data for 4s-p and 5s-p impurities. One observes that the theoretical curves with $\lambda = 0.40$ and $\lambda = 0.20$ are in good agreement with the experimental data. For large Z_{imp}, however, some discrepancies appear which are associated to the common limitations of such local potential models: one needs more refined models where non-local effects are fully taken into account[17].

In the case of noble impurities, we have verified that no bound states arise and one has:

$$\tilde{m}(0;\lambda) = \sum_{\sigma} \sigma \int_{E_b}^{E_F} \tilde{\rho}_{\sigma}(E;\lambda)\, dE. \tag{15}$$

Since $V_0 \gg \lambda\epsilon_c$, one can expand the SK perturbed local density of states $\rho_\sigma(E:\lambda)$ to first order in ϵ_c. Then the local magnetization becomes:

$$m(0;\lambda) = \tilde{m}_{ch}(0) - \lambda\epsilon_c \frac{\partial \tilde{n}_{ch}(0)}{\partial V_0} \tag{16}$$

where

$$\tilde{n}_{ch}(0) = \sum_{\sigma} \int_{E_b}^{E_F} \frac{\rho_\sigma(E)\, dE}{[1 - V_0 F_\sigma(E)]^2 + [\pi V_0 \rho_\sigma(E)]^2} \tag{17}$$

and

$$\tilde{m}_{ch}(0) = \sum_{\sigma} \sigma \int_{E_b}^{E_F} \frac{\rho_\sigma(E)\, dE}{[1 - V_0 F_\sigma(E)]^2 + [\pi V_0 \rho_\sigma(E)]^2} \tag{18}$$

denotes respectively the local occupation number and local magnetization due to a purely electrostatic charge potential V_0. It should be noticed that, since $\tilde{m}_{ch}(0)$ and $\partial\tilde{n}_{ch}(0)/\partial V_0$ have always the same sign and that both λ and ϵ_c are positive quantities, $\tilde{m}(0;\lambda)$ diminishes when λ increases. For isoelectronic noble impurities $\tilde{m}_{ch}(0)$ is also necessary, since the effect of the periods equally modifies the up and down occupation numbers. So, different local magnetic moments arise from different values for λ, which therefore accounts for periodic effects. In fact since the non magnetic impurity disturbs the electron gas, thus changing this transferred magnetization, the σ-electron "feels" a different local exchange splitting $\epsilon_0 = \lambda\epsilon_c$, depending on the nature of the inner core shell levels involved. Invoking pseudopotential arguments[18] one may argue that the electronic screening around an impurity does not depend uniquely on the charge difference between impurity and conduction electrons of the host, but also on the impurity periodic table row. So, in our model, λ describes such periodic effects. For instance, considering the isoelectronic noble elements, in going from Cu to Au, one passes from an inner $3d^{10}$ configuration to a $5d^{10}$ one. Thereby, the local disturbance created by these inner shells with respect to the s-p conduction band is greater when one consider the CuGd system as compared with the AuGd system, and one must have $\lambda(Cu) > \lambda(Ag) > \lambda(Au)$.

In fact, from our self-consistent calculations, adopting $\lambda(Cu) = 0.40$, $\lambda(Ag) = 0.20$ and $\lambda(Au) = 0.10$, one obtains:

$$\frac{\tilde{m}_{Au}(0)}{\tilde{m}_{Ag}(0)} = 1.05 \text{ and } \frac{\tilde{m}_{Au}(0)}{\tilde{m}_{Cu}(0)} = 2.2,$$

and the calculated hyperfines fields reproduce quite well the measured hyperfine fields, as can be seen in figure 2.

In order to test the consistency of our model, we have considered Cu and Ag as being respectively the first 4s-p and 5s-p impurity elements ($Z_{imp} = 1$ in Fig. 1).

In conclusion, we have discussed in the present Section a phenomenological model, which is based on the Daniel-Friedel concept of scattering of spin polarized conduction electrons at the impurity potential.

In spite of the simplicity of our model and without questioning the importance of **ab initio** calculations such as those performed by Kanamori and coworkers[19] and Lindgren[20] for non-magnetic impurites placed in Fe and Ni, one expects from the rather good agreement between theoretical calculations and available experimental data, that the main physical aspects of the problem have been properly taken into account. Some of these are: the role of the 4f-Gd spins in transfering polarization (via a RKKY-type interaction), the s-d induced anti-parallel polarization between d- and s-p conduction bands and principally the role of the parameter λ to describe the period effects.

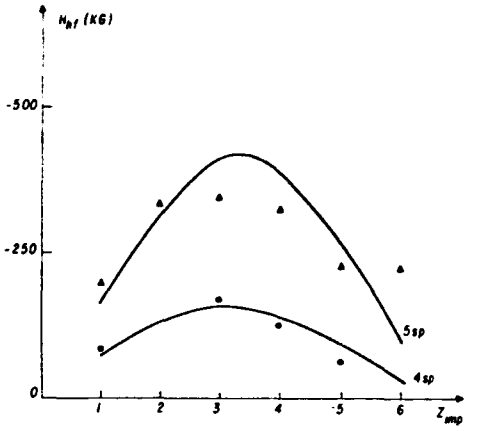

Fig. 1 – Numerical results for the CEP hyperfine at 4s-p and 5s-p impurities in Gd metal, calculated with $\lambda = 0.40$ and $\lambda = 0.20$ respectively. The filled circles represent the experimental data for 4s-p impurities[15] and the filled triangles represent the experimental data for 5 s-p impurities[11]. $Z_{imp} = 1$ means Cu and Ag noble impurities belonging respectively to the 4 s-p and 5 s-p series.

4. LOCAL MOMENTS OF d-IMPURITIES IN Gd

The sign and magnitude of the magnetic hyperfine fields at d-transition impurity nuclei placed in Gd metal are determined by a combination of contributions arising from both conduction electron polarization (CEP) and core polarization (CP) fields[21]. The CEP field, which is due to the polarization of s-p conduction electrons, is given similarly to equation (14), by:

$$H_{hf}^{(sp)} = A(Z)\,\tilde{m}_c(0). \tag{19}$$

The CP field arises from the localized d-magnetic moment of the impurity which polarizes the impurity electron core. It can be written as

$$H_{hf}^{(d)} = -A_{cp}^{(d)}\,\tilde{m}_d(0) \tag{20}$$

where $A_{cp}^{(d)}$ is a positive core polarization coupling parameter, which is constant for a given n-d series[13], and $\tilde{m}_d(0)$ is the d-magnetization at the impurity site. The total magnetic hyperfine field is

$$H_{hf} = H_{hf}^{(sp)} + H_{hf}^{(d)}. \tag{21}$$

So, the local impurity magnetic moment can be estimated from the total hyperfine field, if the CEP contribution and the core polarization coupling constant are known.

In order to explain the hyperfine field systematics, Campbell[22] argued that the principal interaction between Gd ions is due to a direct d-d mechanism. This neglects the RKKY interaction between Gd 4f-spins. The proposal is based on Moriya[23] rules. Thus if one regards Gd as a transition metal at the beginning of a transition series, one expects always a sign reversal in the magnetic moments when one goes from the first to the second half of the n d series. These predictions agree qualitatively for the 3d-impurities. On the other hand, for 5d- and 4d-impurities, relevant discrepancies are observerd. In particular, all 5d-impurities which are placed in Gd metal have negative moments, with the possible exception of Lu.

In this section we suggest that an extended RKKY picture can describe adequately the hyperfine field systematics of d-transition impurities embedded in Gd. In this way, one brings out the fundamental role played by the 4f-moments in driving the ferromagnetic properties of Gd host as well as the transition-like band character of ferromagnetic Gd.

When the d-transition impurity is placed in a Gd substitutional site, it introduces a localized Hartree-Fock spin-dependent potential. One assumes here that such perturbation can be described by effective intraband potentials $V_{c\sigma}$ and $V_{d\sigma}$ acting respectively on the s-p and on the d-conduction electrons[2]. These potentials are determined self-consistently through Friedel sume rule[16], [cf.eq. (6)].

The localized potential $V_{c\sigma}$ is of a Daniel-Friedel type, as described in the previous Sect. [cf. eq. (8)].

The localized potential $V_{d\sigma}$ is written in a Hartree-Fock approximations as

$$V_{d\sigma} = V_{0d} + \sigma\lambda_d\,\epsilon_d + \Delta U\tilde{n}_{d-\sigma}(0). \tag{22}$$

V_{0d} is a purely electrostatic potential arising from the charge difference between impurity d-electrons and host d-conducting electrons. ϵ_d is the host d-band splitting and ΔU is the difference of Coulomb-type correlations at the d-transition site between impurity and host ($\Delta U = U_i - U_h$). One has always $U_i > U_h$ and $\Delta U_{3d} > \Delta U_{4d} > \Delta U_{5d}$. $\tilde{n}_{d-\sigma}(0)$ is the number of d-electrons with spin $-\sigma$ at the impurity site. In the case of d-band splitting, one considers $\lambda_d \cong 1$[2].

The number of α-electrons with spin σ at the d-impurity site, which arises from both extended states and

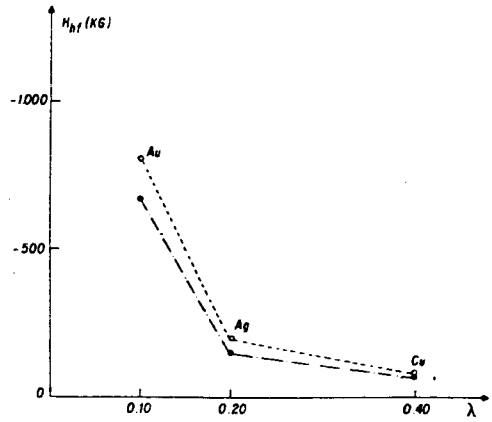

Fig. 2 – Numerical results (empty circles) for the CEP hyperfine field on noble impurities in Gd metal, calculated with $\lambda(Cu) = 0.40$, $\lambda(Ag) = .020$ and $\lambda(Au) = 0.10$. The experimental points 11,15 are given by filled circles.

bound states (case of d-d scattering), $\tilde{n}_{\alpha\sigma}(0)$, ($\alpha$ = d or s-p) is given by an expression similar to eq. (7). Once $\tilde{n}_{\alpha\sigma}(0)$ is obtained, one gets the local magnetizations $\tilde{m}_{\alpha}(0)$, [cf.eq. (13)] and then from eqs. (19) and (20), one obtains the CEP and the CP contributions to the hyperfine field.

The self-consistent numerical results for the CEP hyperfine field and for the CP hyperfine field are shown in fig. 3 (case of 3d-impurities) and in fig. 4 (case of 5d--impurities). One observes in both figures that the theoretical curve for the hyperfine field is in good agreement with the available experimental data. Our calculation for the 3d-impurities exhibits the same trend observed experimentally, with a serious disagreement in the system CrGd, where our total hyperfine field reaches a rather large positive value.

As far 5d-impurities is concerned, one observes also that the theoretical curve for the hyperfine field obtained in the framework of an extended RKKY picture is in good agreement with experimental data. The discrepancy observed for OsGd[24] can be attributed to the small radius of this impurity; therefore such probe tends to occupy an interstitial site rather then an substitutional one[25], and our model does not apply to this case. Moreover, the local 5d-magnetic moments $\tilde{m}_d(0)$, qualitatively agree with the experimental estimates. In particular, $\tilde{m}_d(0)$ reaches its maximum negative value at Re impurity, wherever for Ir only a small localized moment of about $-0.12\mu_B$ is obtained[21].

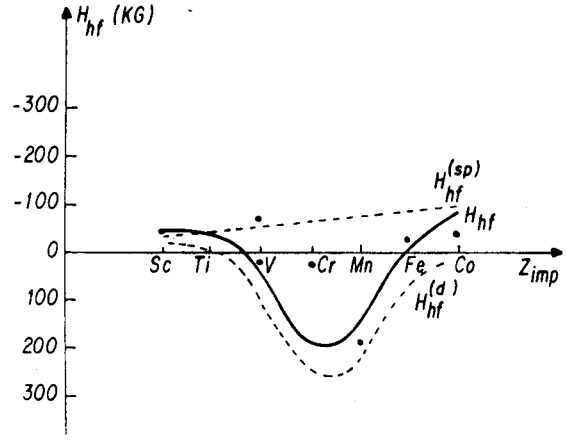

Fig. 3 – Numerical results for the CEP hyperfine field and CP hyperfine field contribution at 3d-transition impurities diluted in Gd host (dotted lines). The full line is the total hyperfine field. We adopted $\lambda_c = 0.40$, $\lambda_d = 1.0$, $\Delta U_{3d} = 0.97$ and $A_{cp}^{(d)} = -125\,kG/\mu_B$. The filled circles represent the experimental data collected from refs. 11, 22, 43 and 44.

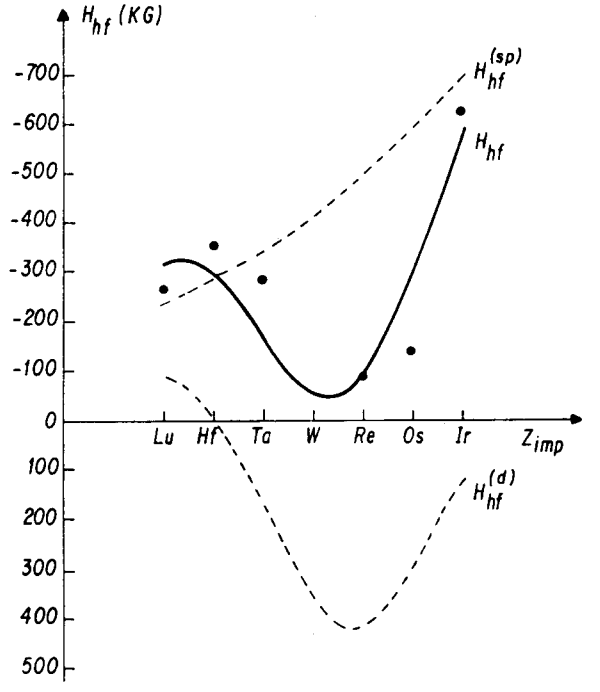

Fig. 4 – Numerical results for the CEP hyperfine field and CP hyperfine field contribution at 5d-transition impurities diluted in Gd host (dotted lines). The full line is the total hyperfine field. We adopted $\lambda_c = 0.2$, $\lambda_d = 1.0$, $\Delta U_{5d} = 0.28$ and $A_{cp}^{(d)} = -1200\,kG/\mu_B$. The filled circles represent the experimental data for the total hyperfine field collected from refs. 11, 13 and 21.

5. LOCAL MOMENT FORMATION AND INTERMEDIATE VALENCE STATE OF ANOMALOUS RARE EARTH IMPURITIES IN Gd.

In this Section we study, via hyperfine field analysis, the local moment formation (local magnetization) in dilute rare earth alloys RGd, where R is an "anomalous" intermediate valence rare earth impurity, such as Ce, Sm, Eu

and Yb placed in a "normal" host like ferromagnetic Gd. From this theoretical discussion we also estimate the valence state of these impurities. In spite that Sm and Tm also exhibit some interesting features in the framework of the intermediate valence phenomena[26,27], we only briefly comment the case of SmGd and we do not discuss the case of TmGd, because there is not yet enough systematic experimental information about these dilute alloys.

It is well known that the rare earth metals can be divided into two groups[26]:

- The "normal" rare earths which have a valency equal to 3 and an integral member of $4f^n$ electrons, independent of pressure and temperature. They are described by the "ionic model", i.e., a collection of N rare earth ions with the $4f^n$ configuration immersed in a sea of 3N conduction electrons:

- The "anomalous" rare earths which have a valency different than 3 and a fractional number of 4f electrons, which can vary with pressure and temperature. It should be noted that chemists described early in the thirties some cases of rare earths with fractional valencies[28]. They obtained the valencies from lattice parameter measurements; for instance, the anomalously large atomic volume of Yb and Eu were ascribed to a divalency of the 4f-shell, due to a special stability by exchange of filled or half-filled 4f-shells. Similarly, the anomalies observed in Ce metal were related to a partial filling of its 4f-shells, giving a valence state larger than 3.

The chemists picture, – an admixture of atoms of different valencies –, although acceptable at high temperatures, cannot adequately describe the phenomena at low temperature. Friedel[29] and Rocher[30] pointed out that this quantum effect occurs because of one of the degrees of ionization of the f-shell would have an energy comparable with the Fermi energy, i.e., one has a narrow 4f-shell close to the Fermi level which produces a large resonance scattering effect. In this case the "ionic model" is no more valid and we use generally the "virtual bound state model" (or "resonance scattering model")[30,31], generally described by the Anderson Hamiltonian[32].

The same duality existis in alloys with rare earth impurities: the "ionic model" can describe alloys with normal rare earth impurities[33,34], whereas the "resonant scattering model" is used for alloys containing anomalous rare earth impurities[26,30,31].

It has been commonly accepted among physicists working in the intermediate valence problem, and not necessarily consistent with the chemists definition of valence, to define the valence state in mettalic systems as equal of the number of conduction (itinerant) electrons[26,27]. Hence, in almost all rare earth based systems, the nominal valence state is 3, corresponding to three itinerant electrons per atom ($5d^1 6s^2$ is the "atomic description"). On the other hand, in mixed-valent Ce-based systems, the valence state is found with non-integer values between 3 and 4, whereas in Sm, Eu, Tm and Yb – based systems it lies between 2 and 3.

It should be noted that hyperfine studies have not been adequately exploited in the study of intermediate valence systems. Particularly useful and intrinsic to their nature is the capability of examining extremely diluted concentrations of 4f- ions as well as local environment effects (i.e., interaction between host and impurity).

In what follows we try to discuss some available hyperfine data on RGd dilute alloys, (R=Ce, Sm, Eu, Yb) trying to insert these systems in the hyperfine systematics of 5d-impurities placed in Gd host as well as to account to the peculiarities of the ferromagnetism of Gd metal and to the anomalous nature of such rare earth impurities.

We start discussing the CeGd system[4]. The technique of time differential perturbed $\gamma - \gamma$ angular correlations (TDPAC) has been widely used in the last years to obtain new information about the formation of local magnetic moments of Ce impurities in metallic elements[35,36,37]. In particular the CeGd system was studied through this technique in the range of the temperatures from 4.2 K up to 242.3 K[35]. The major advantages of TDPAC are that (i) the probes (Ce ions) are located at normal lattice sites and (ii) they may be extremely diluted (concentration $<$ 10 ppm) to a degree where interactions between them can safely be neglected. Nevertheless, through TDPAC one cannot obtain the sign of the hyperfine field. Further, the measured Larmor frequency (2850 MHz extrapolated for T = 0 K, is rather smaller than one should expect for a Ce^{3+} ion (9500 MHz for T = 0 K), thus suggesting that the single Ce ion placed in the Gd metallic host is in an intermediate valence (IV) state.

We assume that in an IV regime, the Ce 4f level ϵ_f, which is fractionally occupied, is strongly admixed with the host conducting states and lies very close to the Fermi energy of the system, i.e., $E_F - \epsilon_f < \Delta$, Δ being the 4f resonance width. Within this picture, Ce ion and Gd host cannot be decoupled and treated as well-separated sytems, the interaction between them (hybridization between the Ce ion and Gd conduction band) being treated perturbatively, as discussed recently by Foglio[38] and Floglio and Schlottman[39].

The 4f resonance in the local density of states ("impurity" site), introduces an extra contribution to the core polarization (CP) hyperfine field. This is because one has a local f magnetization $\tilde{m}_f(0)$. Making the same assumptions as done before to consider the measured hyperfine field systematics of n-d impurities in Gd (n = 3, 4, 5), we use the measured hyperfine field by Thiel et al[35] to calculate self-consistently the Ce valence state $5d^{1+\delta}6s^2$, where δ is the amount of charge transferred to the 5d conduction band, by the Ce 4f level. The extra core polarization field, is due to the occurence of a d-f transferred local f magnetization $\tilde{m}_f(0)$. One has

$$H_{hf}^{(f)} = -A_{cp}^{(4f)} \tilde{m}_f(0). \qquad (23)$$

$A_{cp}^{(4f)}$ is a positive constant, the value adopted here being

$A_{cp}^{(4f)} = 1.500\,\mu_B^{-1}\,kOe^4$. So, the total hyperfine field is given by

$$H_{hf} = A(Z)\tilde{m}_c(0) - A_{cp}^{(5d)}\tilde{m}_d(0) - A_{cp}^{(4f)}\tilde{m}_f(0). \quad (24)$$

A table of coeffients A(Z) is given by Campbell[13], and one can interpolate linearly between the La and Lu coefficients; one finds for Ce the value A(Z) = $= 3.23\times10^3 \mu_B^{-1}$kOe, whereas $A_{cp}^{(5d)}$ is a positive constant of the order of $1200\mu_B^{-1}$kOe for the 5d series[13]. As far as the d-f transferred magnetization is concerned, one can show that $\tilde{m}_f(0)$ is parallel to $\tilde{m}_d(0)$ (see the Appendix of ref. 4):

$$\tilde{m}_f(0) = \zeta_{df}\tilde{m}_d(0) = U_{df}\rho_f(E_F)\tilde{m}_d(0), \quad (25)$$

where U_{df} is an effective d-f Coulomb-type correlation between d and f electrons and $\rho_f(E_F)$ is the density os states of the f resonance at the Fermi energy.

Thus the total hyperfine field is given by:

$$H_{hf} = A(Z)\tilde{m}_c(0) - A_{cp}^{(5d)}\left[1 + \left(A_{cp}^{(4f)}/A_{cp}^{(5d)}\right)\zeta_{df}\right]\tilde{m}_d(0). \quad (26)$$

The calculation of $\tilde{m}_c(0)$ and $\tilde{m}_d(0)$ are obtained following the same procedures in the previous Section.

From recent claims in the literature, the Ce valence in an IV state lies in the interval (3.2, 3.4)[40,41]. This implies, within our picture, that 0.2 – 0.4 f-electrons are transferred to the d band and should be screened via an equation similar to eq. (6), thus fixing a local d-magnetization $\tilde{m}_d(0)$ [cf.eq. (13)]. Therefore, the total hyperfine field is fixed whence ζ_{df} is specified, since all the other terms in Eq. (26) are known, if one adopts the same parameters of the previous Section. We have then taken reasonable values for $\zeta_{df} = U_{df}\rho_f(E_F)$ in order to obtain agreement with the experimental values for the hyperfine field. A good choice for which accounts for the narrow and high density of states of the f resonance $\rho_f(E_F)$ and for the strong effective d-f correlation U_{df} is $\zeta_{df} = 3.6$. This choice yields for T = OK a total negative hyperfine field $H_{hf} = -537$kOe, in a good agreement with the value estimated by Thiel et al[35] ($|H_{hf}| = 540$kOe) and with the whole systematics of hyperfine field data of 5d-impurities diluted in Gd, which are always negative[21]. The valence state v for Ce impurity, implied by the choice $\zeta_{df} = 3.6$ is v = 3.25, which is consistent with refs. 40 and 41. The self-consistently calculated local magnetizations are $\tilde{m}_c(0) = 0.056\mu_B$ and $\tilde{m}_d(0) = 0.054\mu_B$. As far as the temperature dependence is concerned, we refer the reader to ref. 4, where a complete discussion is performed.

The hyperfine field of dilute Yb in Gd, has been determined from Mossbauer experiments to be H_{hf}(YbGd) = $= -280$ (10)kOe[21]. Examination of the temperature dependence of the spectrum yielded no change between 1.6 and 40K. In ref. 21, the authors argued that the values of the hyperfine field, together with isomer shift measurements (0.13mm/s), support the assumption that Yb diluted in Gd metal is in a 2^+ state, i.e., in a $4f^{14}\ 5d^0\ 6s^2$ configuration and has no f moment.

If one adopts the same interpolation as used before to calculate the Ce contact hyperfine coupling, we find the following value for the Yb contact coupling parameter: $A(Z) = 4.67\times10^3\mu_B^{-1}$kOe. Using the same s-p local magnetization calculated for CeGd, since in both Ce and Yb cases one has the same $6s^2$ ionic configuration, one gets: $H_{hf} = H_{hf}^{sp} = -260$kOe, which agrees quite well with the experimental value and remains constant in the whole range of measured temperatures, due to the flatness of the Gd s-p conduction band.

As far EuGd system is concerned, the hyperfine field, determined from Mössbauer experiments is H_{hf}(EuGd) = $= -290(35)$kOe[11]. The Fermi-Segrè contact parameter in this case is: $A(Z) = 3.84\times10^3\mu_B^{-1}$kOe and the local s-p magnetic moment is the same as in YbGd alloy, since the divalent Eu ionic configuration is $4f^7 6s^2$. So, $\tilde{m}_c(0) = 0.056\mu_B$ and hence the CEP hyperfine field contributes $H_{hf}^{(sp)} = -215$kOe. One assumes that, the extra contribution $\Delta H_{hf} = H_{hf} - H_{hf}^{(sp)} = -75$kOe, which is a CP one, arises from the "promotion" of a fraction of an Eu 4f-electron to the Gd 5d-conduction band. This extra CP field, can be written as [cf.eqs. (23) and (24)]:

$$\Delta H_{hf} = H_{hf}^{(f)} = -A_{cp}^{(f)}\tilde{m}_f(0) = -A_{cp}^{(f)}\zeta_{df}\tilde{m}_d(0) = -75\text{kOe}, \quad (27)$$

yielding a d-local moment, $\tilde{m}_d(0) = 0.014\mu_B$. This corresponds to a 4f→5d "charge transfer" v = 0.06 and therefore the Eu valence state is 2.06, i.e., Eu impurity in EuGd is nearly in the Eu^{2+} configuration.

The same picture seems to hold for diluted SmGd systems, where the hyperfine field was obtained through the ion implantation perturbed-angular-correlation technique (IMPACT), in spite that the only available experimental data was obtained at T = 110°K. In this case, one has $H_{hf} = -295(30)$kOe[42]. The CEP hyperfine contribution is $H_{hf}^{(sp)} = -201$kOe, since $A(Z) = 359\times10^3\mu_B^{-1}$ and the local s-p magnetization corresponding to the Sm^{2+} ionic configuration $4f^6 6s^2$ leads also to $\tilde{m}_c(0) = -0.056\mu_B$. Again, the extra hyperfine field $\Delta H_{hf} = H_{hf}^{(f)} = -94$kOe, yields, similarly to the EuGd case, to a d-local moment $\tilde{m}_d(0) = 0.017\mu_B$, corresponding to a 4f→5d "charge transfer" of about v = 0.08. Hence the Sm valence state in the SmGd system is 2.08.

Thus, the self-consistently calculated 4f(impurity) 5d (host conduction band) screened "charge transfer" in RGd dilute alloys (R = Ce, Sm, Eu and Yb) is $v_{Ce} = 0.25$; $v_{Sm} = 0.06$, $v_{Eu} = 0.8$, $v_{Yb} = 0$; i.e, $v_{Ce} > v_{Sm} > v_{Eu} > v_{Yb} = 0$. This is a quite reasonable result, since intermediate valency in these systems may be understood as resulting from a competition between the atomic Hund's rule energy, which favors the $4f^{n+1}$ $(5d6s)^2$ valence state, and metallic host effects, which favor the tendency towards the $4f^n$ $(5d6s)^3$ valence state. This last effect is because of the increase in the impurity-host hybridization and bonding energy provided by the "extra" conduction electron. We can also conclude that the divalent $4f^{n+1}$ (or nearly divalent) valence state is particularly preferable when the 4f-shell is nearly half-filled (Sm, Eu) or nearly filled (Yb), because perhaps to the strong enhancement of the intraatomic correlation effects.

In conclusion, we have studied in this work a large variety of Gd-based dilute alloys (s-p, noble, transition and anomalous rare earth impurities) form the hyperfine field point of view, obtaining a good agreement betwen theoretical calculations, based on very simple models and available experimental data. As a consequence of such calculations, we were able to estimate the local moment formation and retention at the impurity sites. Moroever, we have shown that it is possible to obtain the valence state in the case of anomalous rare earth impurities, even in the very dilute limit. This is in agreement with recent claims in the literature concerning the Ce valence state[40,41]. We also exhibited a tendency which is quite acceptable from general theoretical grounds.

It would be interesting to obtain further systematic hyperfine data, for the large variety of impurities discussed throughout this paper, in other ferromagnetic rare earth hosts like Er, Dy and Tb in order to best test and clarify our models.

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