Local magnetic moments and intermediate valence state of cerium impurities in ferromagnetic rare-earth metals

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Using experimental data for magnetic hyperfine fields obtained through the technique of time differential perturbed $\gamma-\gamma$ angular correlations (TDPAC) in the highly diluted system Ce*R* (R=Gd, Tb), we theoretically discuss the formation of the local moments at the Ce impurity site, adopting an intermediate valence model. The ferromagnetic rare-earth host is considered as a transition metal in the beginning of a 5*d* series and the Ce*R* alloys are described as strongly $d-f$ correlated and hybridized systems. One calculates the hyperfine field which reproduces quite well the experimental data. The Ce valence in these systems is also obtained, giving values in good agreement with experimental results and theoretical claims involving Gd and Tb band calculations. Some comments about the diluted systems Yb*R* (R=Gd, Tb) are also made.

At the present very extensive experimental data on the hyperfine fields at the sites of diluted $n-d$ transition impurity ions (n=3,4) in ferromagnetic Gd are available in the literature.[1] More recently, Boysen *et al.*[2] reported systematic experimental hyperfine data of diluted 3*d* ions in ferromagnetic Tb and also some hyperfine data of diluted 5*d* ions in this same host were obtained.[3] From the measured magnetic hyperfine fields in these locally perturbed rare-earth hosts one can estimate the local magnetic moments formed at the impurity sites. For instance, the local magnetic moments change sign when one goes from the first-half to the second-half of the 3*d* series.[1,2,4,5]

In order to explain these data, it has been invoked[2,4] that the main interaction between rare-earth host ions (Gd or Tb) is due to a direct $d-d$ mechanism, thus neglecting the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction between rare-earth 4*f* moments. The proposal is based on Moriya[6] rules: if one regards a ferromagnetic rare-earth host like Gd or Tb as a transition metal in the beginning of a 5*d* series, one always should expect a sign reversal in the local moments when one passes from the first- to second-half of the $n-d$ series. These predictions agree qualitatively for the case of 3*d* impurities. On the other hand, all 5*d* impurities diluted in Gd have negative moments (with the possible exception of Lu)[6] and the available data of 5*d* ions diluted in Tb (e.g., Ta*Tb* and Ir*Tb*) show a total negative magnetic hyperfine field and small negative moments.[3,5]

So, it was suggested that an alternative theoretical approach[5–7] based on an extended RKKY picture which can describe adequately the hyperfine field systematics of all *d*-transition impurities placed in the heavy ferromagnetic hosts Gd and Tb. This picture brings out the fundamental role played by the 4*f* moments in driving the ferromagnetic properties of these metals and takes into account properly the transition metal-like character of these materials, i.e., the existence of conducting *s* and *d* bands. Within this picture, we explained adequately the hyperfine field systematics of the *d* impurities placed in Gd and Tb.

In this work we want to discuss some available hyperfine field data on Ce*R* and Yb*R* (R=Gd, Tb) alloys trying to insert them in the hyperfine field systematics of 5*d* impurities placed in these rare-earth hosts. Experimental results concerning isomer shifts of the 5*d* Mössbauer element ^{193}Ir diluted in Gd and Tb show that they are nearly constant, the value of 2 mm/s being in good agreement with the systematic of isomer shifts of ^{193}Ir in 5*d* transition metal hosts.[3,8] The same feature of almost constant isomer shifts is obtained for the 3*d* Mössbauer element Fe placed in Fe*R* (R=Gd, Tb).[2,9] This suggests that the host $s-p$ and *d*-band occupations are quite the same for these rare-earth metals. Band calculations[10,11] have shown indeed that Gd and Tb exhibit *d* bands contributing a high density of states around the Fermi level.

One can estimate[7] from the above-mentioned band calculations the *d*- and $s-p$ band occupation numbers for both metals as being, respectively, $\langle n_d\rangle$=2.2 electrons (per host atom) and $\langle n_c\rangle$=0.8 electrons (per host atom) giving a 3^+ configuration: $\langle n_d\rangle+\langle n_c\rangle$=3.0 electrons (per host atom). Gd is the only rare-earth metal which goes directly from the paramagnetic phase to the ferromagnetic one with a Curie temperature T_C equal to 298 K. The saturation magnetic moment at very low temperature is $7.63\mu_B$ which is larger than the $7\mu_B$ value corresponding to the trivalent Gd^{3+}. Tb metal undergoes two magnetic transitions characterized by the Néel temperature T_N (T_N=229 K) and the Curie temperature T_C (T_C=221 K) and at very low temperature the saturation magnetic moment is $9.34\mu_B$, which has to be compared to the theoretical value of $9\mu_B$, expected for the trivalent ion Tb^{3+}.

The ferromagnetism of these "normal" rare-earth metals is described in a simple Stoner-type picture by two *d*-spin subbands split by and exchange energy, driven mainly from the exchange interaction between the effective 4*f* moment and the *d* electrons. Moreover, one assumes that, due to host hybridization, the $s-p$ and *d*-conduction bands have antiparallel magnetizations, as occur in Fe metal.[5,6,12]

 0021-8979/94/75(10)/6737/3/$6.00

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.[13] In particular the CeR (R=Gd, Tb) systems where studied through this technique by Thiel *et al.*,[14,15] suggested that the single Ce ion in CeR systems (R=Gd, Tb) 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 host conduction 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. The magnetic hyperfine field at rare-earth impurity nuclei placed in Gd or Tb metals is determined by a combination arising from both conduction electron polarization (CEP) and core polarization (CP) fields. The CEP field, which is due to the polarization of $s-p$ conduction electrons, is given by

$$H_{\rm hf}^{(sp)}=A(Z)\tilde{m}_c(0)\ , \tag{1}$$

where $A(Z)$ is the hyperfine contact parameter[16] and $\tilde{m}_c(0)$ is the $s-p$ magnetization at the impurity site. Using Campbell's data[16] for La and Lu one gets for Ce the value $A(Z)=3.23\times10^3\ \mu_B^{-1}$ kOe. Due to the $5d$ character ascribed to the anomalous rare-earth Ce impurity, a CP arises from its localized d-magnetic moment which polarizes the impurity electron core, similar to the case of a transition element impurity. It can be written as

$$H_{\rm hf}^{(d)}=-A_{\rm CP}^{(5d)}\tilde{m}_d(0)\ , \tag{2}$$

where $A_{\rm CP}^{(5d)}$ is a positive CP coupling parameter, of the order of $1200\mu_B^{-1}$ kOE for the $5d$ series and $\tilde{m}_d(0)$ is the d magnetization at the impurity site. The $4f$ resonance in the local density of states ("impurity site") introduces an extra contribution to the CP hyperfine field. This extra CP hyperfine field is due to the occurrence of a $d-f$ transferred local f magnetization $\tilde{m}_f(0)$.[12] One has

$$H_{\rm hf}^{(f)}=-A_{\rm CP}^{(4f)}\tilde{m}_f(0)\ , \tag{3}$$

where $A_{\rm CP}^{(4f)}$ is a positive coupling constant, the value adopted here being 1500 μ_B^{-1} kOe.

The total hyperfine field is then

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

In Ref. 12 it is shown that $\tilde{m}_f(0)$ is parallel to $\tilde{m}_d(0)$:

$$\tilde{m}_f(0)=\xi_{df}\tilde{m}_d(0)=U_{df}\rho_f(E_F)\tilde{m}_d(0)\ , \tag{5}$$

where U_{df} is an effective $d-f$ Coulomb type interaction and $\rho_f(E_F)$ is the density of states of the $4f$ resonance at the Fermi energy. Thus, the total hyperfine field is

$$H_{\rm hf}=A(Z)\tilde{m}_c(0)-A_{\rm CP}^{(5d)}[1+(A_{\rm CP}^{(4f)}/A_{\rm CP}^{(5d)})\xi_{df}]\tilde{m}_d(0)\ . \tag{6}$$

The self-consistent calculation of $\tilde{m}_c(0)$ and $\tilde{m}_d(0)$, which are the solution of a Koster–Slater problem are given in detail in Refs. 5 and 6;

$$\tilde{m}_\alpha(0)=\sum_\sigma \sigma\int_{-\infty}^{\mu}\frac{\rho_{\alpha\sigma}(E)f(E)dE}{[1-V_{\alpha\sigma}F_{\alpha\sigma}(E)]^2+[\pi V_{\alpha\sigma}\rho_{\alpha\sigma}(E)]^2}\ , \tag{7}$$

where $\rho_{\alpha\sigma}(E)$ is the unperturbed density of states of a α subband with spin σ ($\alpha=s-p$ or d), $F_{\alpha\sigma}(E)$ is its Hilbert transform, $f(E)$ is the Fermi Dirac function, and μ is the chemical potential. At $T=0$ K, one has $\mu=E_F$. The localized potentials are self-consistently obtained via the Friedel sum rule

$$\Delta Z^\alpha=\sum_\sigma \Delta Z_\sigma^\alpha(V_{\alpha\sigma})=-\frac{K_\alpha}{\pi}\sum_\sigma \arctan\frac{\pi V_{\alpha\sigma}\rho_{\alpha\sigma}(E_F)}{1-V_{\alpha\sigma}F_{\alpha\sigma}(E_F)}\ , \tag{8}$$

where ΔZ_σ^α is the charge displaced by the potential $V_{\alpha\sigma}$ in the σ subband of α electrons and K_c accounts for degeneracy; one has $K_c=4$ and $K_d=5$.

Let us now focus our attention to the CeGd system. It is believed that the Ce valence in an IV state lies in the range (3.2–3.4). This implies in our picture that ν electrons in the range 0.2–0.4 are transferred to the d band and are screened via Eq. (8), thus fixing a local d magnetization $\tilde{m}_d(0)$ obtained through Eq. (7). Thus, the total hyperfine field is fixed when ξ_{df} is specified, since all the other terms in Eq. (6) are known if one adopts the same parameters of Refs. 5 and 6. We adopted for $\xi_{df}=U_{df}\rho_f(E_F)$ the value $\xi_{df}=3.6$. This choice yields for $T=0$ K a total negative hyperfine field $H_{\rm hf}=-537$ kOe which is in good agreement with the value obtained by Thiel *et al.*[14] which is: $|H_{\rm hf}|=540$ kOe and with the whole systematic of $5d$ impurities diluted in Gd which are always negative. The choice $\xi_{df}=3.6$ yields a valence state of 3.25 ($\nu=0.25$) and therefore the Ce configuration is $4f^{0.75}\ 5d^{1.25}\ 6s^2$, which is consistent with the results obtained in Ref. 17. The self-consistently calculated local moments are $\tilde{m}_c(0)=-0.056\mu_B$ and $\tilde{m}_d(0)=0.054\mu_B$.

Let us now discuss the CeTb system. At $T=0$ K, the experimental value estimated for the total hyperfine field is:[15] $H_{\rm hf}-550$ (80) kOe. Assuming that the Ce valence state in CeTb is the same as in CeGd, i.e., $\nu=0.25$, our calculated self-consistent local moments are $\tilde{m}_c(0)=-0.0314\mu_B$ and $\tilde{m}_d=0.0280\mu_B$. In order to fit the experimental value one adopts $\xi_{df}=9.86$ and then one obtains: $H_{\rm hf}=-543$ kOe at $T=0$ K, in good agreement with the experimental result. Notice that ξ_{df} accounts for the high density of states of the f resonance $\rho_f(E_F)$ at the Fermi level and for the strong effective $d-f$ correlation and so one can make a comparison between the adopted values of ξ_{df} for CeGd and CeTb. One has

$$\frac{\xi_{df}({\rm Ce}Tb)}{\xi_{df}({\rm Ce}Gd)}=\frac{9.86}{3.60}=2.74\ . \tag{9}$$

Remembering that $\xi_{df}=U_{df}\rho_f(E_F)$ and assuming that U_{df} is almost the same for both systems and that $\rho_f(E_F)$ is roughly proportional to the d peak of the density of states at the Fermi level of the hosts, one has

$$\frac{\xi_{df}(\mathrm{Ce}Tb)}{\xi_{df}(\mathrm{Ce}Gd)} \simeq \frac{\rho_d^{\mathrm{Tb}}(E_F)}{\rho_d^{\mathrm{Gd}}(E_F)} . \tag{10}$$

From band calculations[10,11] one has $\rho_d^{\mathrm{Tb}}(E_F)=66$ states per atom per Rydberg whereas $\rho_d^{\mathrm{Gd}}(E_F)=25$ states per atom per Rydberg; thus $[\rho_d^{\mathrm{Tb}}(E_F)]/[\rho_d^{\mathrm{Gd}}(E_F)]=2.64$, in a good agreement with our adopted values.

The existence of such sharp peaks near the position of the Fermi level are responsible for the steep drop with temperature of the local d magnetizations and therefore of the effective core polarization contributions to the hyperfine field [see the last term in Eq. (6)], whereas the $s-p$ contribution remains almost constant with temperature. This effect should be more dramatic in CeTb than in CeGd as is indeed experimentally verified.[14,15]

As a final comment let us briefly discuss the YbR systems. Yb is an anomalous rare earth with a 2^+ ionic configuration: $4f^{14}\,5d^0 6s^2$. The hyperfine field of Yb embedded in Gd was obtained from Mössbauer experiments yielding the value: $H_{\mathrm{hf}}(\mathrm{Yb}Gd)=-280(10)$ kOe,[18] which is almost temperature independent. These authors argued that the values of the hyperfine field, together with isomer shift measurements, support the assumption that Yb in YbGd is in a 2^+ state and has no f moment. We used the same $s-p$ local magnetization calculated for CeGd, since in both the Ce and Yb cases one has the same $6s^2$ ionic configuration. From Ref. 16 one gets (interpolating between the La and Lu coefficients): $A(Z)=4.67\times10^3\ \mu_B^{-1}$ kOe and then $H_{\mathrm{hf}}=H_{\mathrm{hf}}^{sp}=-260$ kOe, which agrees quite well with the experimental value.

As far as the YbTb system is concerned there are no available experimental hyperfine field measurements. Using the same assumptions as made for YbGd, one can predict the following value for the hyperfine field. $H_{\mathrm{hf}}=H_{\mathrm{hf}}^{sp}=-147$ kOe which should remain almost constant in temperature due to the flatness of the Tb $s-p$ conduction band.

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