Investigation of the different nature of magnetic hyperfine fields of Ce probes in Gd and Co matrices

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Abstract The magnetic hyperfine fields (MHF) acting on ^{140}Ce probes diluted in Gd and Co matrices, measured at low temperatures, were compared with those obtained from first-principles electronic structure calculations. It was found that the origin of the MHF for these two situations is completely different even though the total MHF presents similar values on both the cases. For Ce diluted in Gd, the Ce *4f* shell is localized and the orbital MHF dominates. On the other hand, for Ce probes in Co matrix the Ce *4f* shell is delocalized and, as a consequence, the MHF is dominated by the Fermi-contact contribution.

1 Introduction

One of the main concerns when one studies magnetic hyperfine fields (MHF) is to establish a connection between the MHF with the properties of the electronic structure of the atom at which the MHF is determined.

When probe atoms present quenched electronic orbital moment and/or closed electronic shells, only the Fermi contact contribution to the MHF dominates. On the contrary, as frequently happens with the rare-earth probes, a localized partially filled *4f* electron shell is developed and gives rise to a significant or even dominant orbital and spin-dipolar contributions to the MHF.

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In the present study, a comparison is made between experimentally determined MHF acting on Ce probes diluted in Co and Gd matrices with those obtained by first principles electronic structure calculations. Both of these matrices present similar crystal structures and same magnetization orientation at low temperatures. The main difference between these two matrices is the interatomic distance, and thus, they represent an ideal tool to study the effects of the variation of the distance between the Ce probe and matrix atoms on the Ce MHF. As the difference between these two configurations is quite large, the change on the MHF on going from a localized to a delocalized Ce *4f* electronic state can be studied in detail.

It was found that although these two situations lie in extreme Ce *4f* electronic configurations, both, the calculated as well as the measured MHF at low temperatures present coincidentally very similar total values but the nature of the components of these MHF's is completely different.

2 Experimental results

The measurements of the MHF on Ce probes diluted in Gd matrix as a function of temperature were performed by Thiel et al. [1] while similar measurements on Co matrix were carried out by Carbonari et al. [2]. Both the experiments were performed with the time differential perturbed angular correlation spectroscopy employing the $^{140}La \rightarrow {}^{140}Ce$ probe.

On both the cases the temperature dependence of the MHF deviates from the expected Brillouin behavior followed by the magnetization of the specimens. Instead of maintaining a constant saturation value, the Ce MHF begins to increase again as the temperature is decreased further beyond $T \sim T_C/2$, where T_C is the magnetization critical temperature. It is believed that this additional MHF arises from the alignment of the Ce *4f* orbital. [1, 2]

At the lowest measured temperature, around 10 K, the Ce MHF appears to be saturated on both the cases. The resulted MHF values are 51.7 T and 51.9 T, respectively, for Ce diluted in Co and Gd matrices.

3 Details of the calculations

Self consistent electronic structure calculations were performed within the framework of the density functional theory. The employed method was the APW+lo embodied within the WIEN2k computer package [3]. The Gd and Co matrices doped with Ce were simulated by means of super-cells with twice the value of the ordinary hexagonal crystal cell parameters. One of the 16 host atoms within the super-cell was replaced with Ce. Relaxation of forces over the atoms was performed for the case of Co. In this procedure the Ce–Co distance did not change appreciably from the initial distance of 2.50 Å. Some of the Co atoms did move, decreasing the Co-Co distances to the 2.46–2.40 Åinterval. In the case of Gd, no relaxations were performed. The Ce-Gd and Gd-Gd distances were held fixed to 3.57 Å.

In the calculations the muffin-tin radii were $RMT = 2.0, 2.5$ and 2.5 a.u respectively for Co, Gd and Ce. The utilized plane wave cutoff, K_{max}, was given by $RMT_{min} * K_{max} = 7.0$, and the number of k-points within the whole Brilouin zone

was 300 and 900 respectively for the Gd and Co cases. Spin orbit coupling was taken into account and for the exchange and correlation effects, the new hybrid functional B3PW91 was utilized [4] since it greatly improves on the description of highly correlated rare-earth electrons.

4 Discussion

The point group symmetry of Ce probe atoms inserted in Gd or Co matrices is $\bar{6}m2$. Under the effect of a crystalline field with this symmetry, the allowed ground states of Ce *4f* are $|\pm 1/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$. It was found that for the case of Ce diluted in Gd, the populated *4f* state of Ce is the $|\pm 1/2\rangle$ orbital in only one of its spin channels. This give us a good indication that the utilization of the hybrid functional B3PW91 allowed a proper description of the electronic structure of Ce for this case. In the case of Ce in Co, an electronic state is formed that is an admixture of all of the six orbitals.

The difference between these two situations can be seen by comparing the resulted orbital and spin moments of the Ce *4f* shell. In the case of Ce in Gd, both the moments are relatively large and, as a consequence, large values of the orbital MHF and the Ce magnetic moment result, as shown in the Table 1. For this case, the Ce *4f* state is, by far, well localized. This situation is clearly seen in the bottom DOS graph of Fig. 1 where a relatively sharp peak, with atomic-like character, appears due to the Ce *4f* contribution. In contrast, when Ce replaces for a Co atom in Co host matrix, its DOS contribution appears to be spread over a large range of energies and also over both the spin channels, as seen on the top of Fig. 1. In this case the Ce *4f* state is delocalized, as expected. The orbital and spin moments for this case are substantially smaller than that of the former case, as seen in Table 1.

The fact that the spin magnetic moments of Ce appear with opposite signs in the two situations reflects the different coupling mechanisms of atomic moments. Whereas the Ce-Gd coupling is mediated by the Ruderman–Kittel–Kasuya–Yoshida interaction, the Ce-Co is afforded by the direct Co *3d* and Ce *5d* exchange interaction followed by the intra-atomic *5d-4f* exchange interaction, according to the Campbell and Brooks model [5, 6].

Other effects caused by delocalization on the magnitude of the orbital contribution to the MHF and magnetic moments are the small electronic de-population of the Ce *4f* orbitals and an enlargement of the width of the *4f* wave function as shown in Table 1. For the Ce in Co case, the expected value of the $1/r^3$ operator is 2.85 au.$^{-3}$ as compared to 4.31 au.$^{-3}$ for Ce in Gd, giving for the mean *4f* charge density radii $\bar{r}$, respectively 0.37 and 0.33 Å.

The spin-dipolar contribution to the Ce MHF in the case of Ce in Gd is large, 10.8 T, as shown in Table 1. This comes from the fact that the Ce *4f* orbital is localized, producing a large anisotropic spin (and charge) density distribution around the Ce nucleus at a very small distance of only 0.33 Å. On the contrary, for the case of Ce in Co, the Ce *4f* spin-dipolar contribution to the MHF is relatively small owing to the effects already described above: electronic population of both the spin channels and orbitals, as well as average electronic de-population of the entire *4f* shell caused by the delocalization, resulting in a much more isotropic spin (and charge) density distribution.

Table 1 Ce Magnetic hyperfine field components (T), expectation value of the $\frac{1}{r^3}$ operator for the *4f* Ce state (au^{-3}), number of *4f* electrons, Ce and host atom magnetic moments (bohr magneton), for the Co and Gd hosts, resulted from the calculations

	B_c^{val}	B_c^{core}	B_{orb}	B_{dip}	B_{tot}	$\left\lvert B_{exp} \right\rvert$	$\frac{1}{r^3}$	ne_{4f}	μ_{Ce}	μ_{host}
Co	−46.7	5.96	2.16	0.189	−38.5	51.7	2.85	0.85	−0.30	1.1–1.7
Gd	31.6	−33.8	−51.2	10.8	−42.7	51.9	4.31	0.99	1.05	7.2

Only the magnitude of the experimental MHF is known. The cobalt magnetic moment depends on the distance from the Ce probe

Fig. 1 Ce *4f* density of states plot for Ce in Co and Gd matrices. The *dashed line* represents the Fermi level
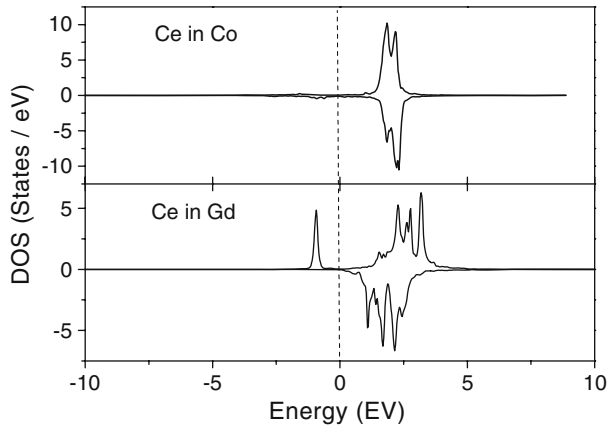
The resulted Fermi-contact fields are also shown in Table 1 and are separated between two contributions, namely, valence and core. The valence contribution here includes the following Ce electronic shells: $5s^2$, $5p^6$, $4f^1$, $5d^1$ and $6s^2$. In the case of Ce in Gd, both, the core and valence electrons are highly polarized but in opposite directions, resulting in a net contact field of only –2.2 T. On the contrary, in the case of Ce in Co, the valence contribution is large, of the same order as in the Gd case, but the core contribution is relatively small. The resultant contact contribution for the Co case is then large, -40.7 T, and comes from the almost vanishing core polarization. This effect can be understood by the lack of a local magnetic moment on Ce *4f* caused by the de-localization.

It is interesting to notice that the total MHF present very similar values. The calculated total fields agree with the experimental values only within ∼ 25% but it can be considered as a reasonable agreement in face of the known limitations of the density functional theory. On the other hand, the very distinct Ce electronic states, with localized nature in Gd case and de-localized in Co appeared naturally with our simulations, as already expected. It can then be concluded that the striking feature of these results is the evidence of the possibility to have two very different electronic configurations that yield similar magnetic hyperfine fields.

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