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Investigation of the Magnetic Hyperfine Field at ^{140}Ce on Gd Sites in $GdCo_2$ Compound

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Abstract. Perturbed angular correlation experiments on ^{140}La–^{140}Ce probes substituting for the Gd positions on $GdCo_2$ demonstrate that the magnetic hyperfine field (MHF) on Ce atoms follows an expected Brillouin function but with a substantially reduced saturation value as compared with the MHF acting on free Ce^{+3} ions. The results were interpreted with the aid of first principles electronic structure calculations showing that the reduced value of the MHF is a consequence of a small orbital contribution to the MHF which was attributed to the de-localization of the Ce 4f electronic state.

Key Words: electronic structure, hyperfine field, rare-earth compounds.

1. Introduction

The $GdCo_2$ belongs to a series of rare earth (*R*) intermetallic compounds where both the rare-earth and Co atoms present magnetic moments exhibiting ferrimagnetic order. In rare earth–transition–metal binary alloys the magnetic properties are determined by the interaction of the magnetic moments of the rare earth 4f electrons with the itinerant 3d electrons of the transition metals. In RCo_2 compounds the 3d magnetization is reached by the local f–d exchange mechanism, i.e., the 4f spins polarize the *R* 5d band which is hybridized with the Co 3d band. The result is an antiparallel ordering of Co atoms relative to the 4f *R* spins.

In this work we present the results of first principles calculations of the magnetic hyperfine field (MHF) acting on cerium probes substituting for Gd in $GdCo_2$. It it is seen that the Ce 4f electrons in this system are de-localized and sense the crystalline field effects that substantially quench the orbital moment [1, 2].

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2. Details of the experiment

The samples were prepared by arc melting the constituent high purity elements under argon atmosphere along with neutron irradiated ^{140}La substituting for 0.1 atom percent of Gd. The TDPAC experiments were performed utilizing the 329–487 keV γ–γ cascade of ^{140}Ce populated from the β decay of ^{140}La. The measurement of the magnetic interaction was performed at the ^{140}Ce 2083 keV level, 4+ spin state. Since the quadrupole moment of this state is known to be very small, no quadrupole interactions are expected. The measurements of the magnetic interactions were performed at the temperature range of 8–400 K with a setup consisting of four BaF2 detectors. The resolution of the detector system was 0.6 μs.

3. Electronic structure calculations

The calculations were performed within the scheme of the density functional theory (DFT). In this formalism [3], all the observables are given as a functional of the electronic density (in our case, the spin densities). In particular, the total energy of the system is given by:

$$E_{tot}\left(\sigma^{\uparrow},\sigma^{\downarrow}\right) = T_s + E_{ee} + E_{Ne} + E_{xc} + E_{NN}. \tag{1}$$

Here, $\sigma^{\uparrow}$ and $\sigma^{\downarrow}$ are the spin densities, T_s the single particle kinetic energy, E_{ee} the Hartree component of the electron–electron interactions, E_{Ne} the nuclei-electron Coulomb interaction, E_{xc} the exchange and correlation energy and E_{NN} the Coulomb nuclei-nuclei interaction energy. The aim in these calculations is to find the spin densities which minimize the energy or, equivalently, to solve the one particle Kohn–Sham equation in a self-consistent way [4]. The method employed here utilizes a basis set consisting of augmented plane waves plus local orbitals (APW + lo) as embodied in the WIEN2k [5] computer package. The main limitation of this method lies in the description of the exchange and correlation energy E_{xc}. The usual approach is the local spin density approximation (LSDA) or the improvements with the generalized gradient approximation (GGA), but both suffer for the improper description of the correlation energy and then especially fails to describe the open d or f electronic shells. The calculations were performed with the experimental value for the GdCo$_2$ cell parameter, namely a = 7.28 Å. The number of plane waves was limited to $k_{\max}$ = 7/RMT, with the muffin–tin radius RMT ~ 2.4 a.u. The charge density was Fourier expanded up to $G_{\max}$ = 14 and, and for the Brillouin zone integrations, a tetrahedral mesh of 1200 k points was utilized. Exchange and correlations effects were treated with generalized gradient corrections [6]. The valence states were treated within the scalar–relativistic approach, taking into account the spin–orbit coupling, while the core states were relaxed in a fully relativistic manner. The calculation of the magnetic hyperfine field, also implemented into the WIEN2k code, was performed following the formulas due to Blügel et al. [7], which include relativistic corrections. The calculations were extended to the Ta and Cd impurities, in order to test for the reliability of the calculations to reproduce the MHF on different electronic configurations of the probes. It is expected that the correlation effects would be small for the f states due to the half-filled shell of Gd, just one f electron in case of Ce and the completely populated shell of Ta.

4. Results and discussion

In Figure 1 it is shown the measured Larmor frequency as a function of temperature for the Ce probes in GdCo$_2$. It can be seen that two distinct sites are occupied by the probes with different values of the MHF. The curve with higher values of MHF is attributed to Ce probes occupying Gd sites in GdCo$_2$ since it follows the Brillouin function with the expected Curie temperature of the compound, $T_C = 395$ K. The saturation value of the MHF, 24.6 T at $T = 8$ K, is substantially smaller than the MHF of isolated Ce^{+3} ions in insulators, namely, H_{hf} (Ce^{+3}) = 192 T. There are two possibilities to interpret the observed small MHF: 1) In GdCo$_2$ the Ce probes sense a large transferred MHF highly compensated by a large orbital contribution to the MHF, since they have opposite signals, or 2) The Ce 4f^1 state senses the crystalline field and partially hybridize with neighboring electronic states and then loses the strictly local character found in insulators. In this case a smaller orbital contribution to the MHF is expected.

In Table I we present the results of the calculations of MHF for Ce, Ta and Cd probes substituting for Gd and for the Gd itself in GdCo$_2$, together with the experimental results taken from reference [8]. It is seen that for Ce probes, the calculated MHF agree quite well with the experiment if it is accepted that both the measured and calculated MHF have the same sign. The result then points to the second possibility stated above, namely, that the orbital contribution to the MHF is small, and thus, the Ce 4f^1 electrons are partially de-localized. The orbital contribution to the Ce MHF resulted to be -10.6 T.

We can see that the Fermi contact contribution is dominant in all the probes. It can also be seen that the model reproduces quite well the MHF in the case of Ce and Ta but not for Cd. Since in this case we expect a very small core polarization, as it is indeed seen in Table I, the failure would be due to the improper description of the Cd 5s electrons. A possible reason for this result is that the super-cell utilized in the calculations is not sufficiently large, enhancing the Cd–Cd interactions in the simulations even though they were performed with eight atomic layers between two Cd atoms. No experimental value for Gd was found in the literature. Comparing Gd and Ce, which differ only on the number of f electrons, a larger MHF results in the case of Gd, with larger valence and core contributions, due to the larger Gd magnetic moment, as expected. On the other hand, these contributions to the MHF have opposite signs resulting in a relatively small total Fermi contact MHF especially in the case of Gd. In this

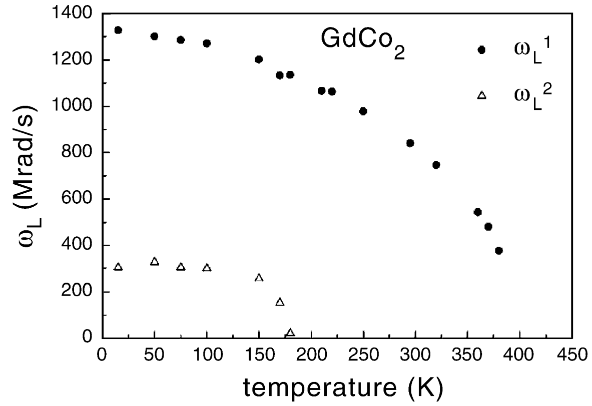

Figure 1. Temperature dependence of the Larmor frequency at ^{140}Ce.

Table I. Calculated and experimental magnetic hyperfine fields at the indicated probes and the Gd site in GdCo$_2$

Probe	Contact	Valence	Core	Orbital	Dipolar	Total	Experiment
Gd	61.0	346.7	−285.7	−3.3	0.38	58.1	–
Ce	33.1	52.3	−19.2	−10.6	0.145	22.4	24.6
Ta	−15.9	−16.6	0.72	−0.27	−0.039	−16.2	19.7
Cd	−34.6	−34.7	0.11		0.0041	−34.6	21.8

Values given in T. Only the magnitude of MHF is given for the experimental value. For the Fermi contact field the valence and core contributions are given in addition.

way, if one imagines a large orbital contribution at the Ce probes, the polarization of valence and core electrons would increase accordingly but not the total contact field. In this case we would expect a large total MHF, being the orbital part the main contribution. This seems not to be the present case, enforcing the argument that the main effect on Ce 4f^1 electrons in this material is de-localization.

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