

DFT-based calculations of the magnetic hyperfine interactions at Cd sites in RCd (R = rare earth) compounds with the FP-LAPW ELK code

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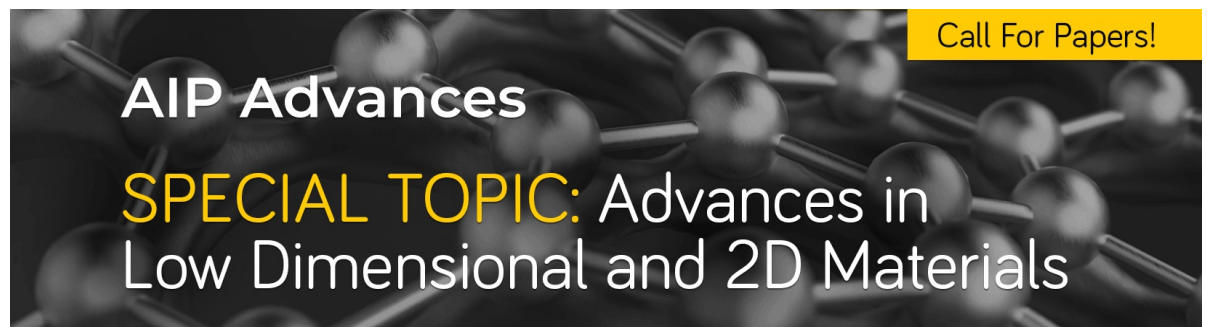
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ABSTRACT

In the work here reported, we have calculated magnetic hyperfine interactions in rare-earth (R) intermetallic compounds by using the free open-source all-electron ELK code. The RCd (R = Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) series was chosen as a test system because an almost complete set of experimental data on the hyperfine parameters at Cd sites was acquired through the time differential perturbed angular correlation (TDPAC) spectroscopy as previously reported. Moreover, results on magnetic hyperfine field (B_{hf}) from WIEN2k code were also reported allowing a qualitative comparison analysis. We emphasize that the utilized version of ELK accounted for the contact field only. Yet, as it is the only contribution expected for Cd site in RCd compounds, the calculated B_{hf} values are in reasonable agreement with the experimental results. The Spin-orbit coupling when taken into account led to a decrease in deviation from experimental data. Addition, the Hubbard-like term was revealed crucial in order to make B_{hf} predictions for CeCd, suggesting that this behavior may be associated with a weaker $4f$ electron localization in Ce.

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I. INTRODUCTION

Magnetic materials present singular properties which have their origin at the atomic level where the electronic contributions play a crucial role throughout.

In particular, hyperfine interactions (nuclei and magnetic and/or electric potentials from electron cloud interactions) investigations provide valuable informations on the parameters that characterizes magnetic systems, for example, magnetic exchange interactions,^{1,2} the order and temperature transition of magnetic phases,^{1,3} the spin-wave excitations,^{4,5} and magnetic relaxation processes⁶ among others.

Although measurements knowledge of those hyperfine fields could give a widely comprehension⁷ about a system, first principles calculations based on the density functional theory (DFT)⁸ are desired to analyse more deeply their outcomes.

In the DFT, the operators at ground state are functional of the electronic density ($\rho(\mathbf{r})$) which is obtained from solving self-consistently a set of equations called Kohn-Sham scheme^{8,9}

Several computer codes based on DFT have been developed to calculate the solid electronic band structure. In this work, we present the magnetic hyperfine field (B_{hf}) at Cd nuclei in RCd compounds (where R is a rare-earth element) evaluated by the free open-source all-electron ELK code¹⁰ and compare the results¹¹ with both experimental values and those calculated by the WIEN2k code.¹²

Elk project was released a few years ago with a user-friendly philosophy and growing significantly since then, despite that, the number of magnetic studies using it is scarce, especially those regarding hyperfine interactions. On the other hand, WIEN2k is one of the most popular codes available and a widespread useful tool to improve magnetic knowledge. Although the two codes use the same

methodology for calculations of B_{hf} ,¹³ this work might shed light in the comparison between their performance and reproducibility on *ab initio* calculations.

Rare-earth (R) elements differ in the number of well-shielded 4f electrons which are responsible for the magnetism in compounds consisting of rare earth element as well as non-magnetic atoms. The main feature of rare-earth elements is that the orbital magnetic contribution is strong in relation to spin and intensively varies with the number of 4f electrons. Such RCd compounds (where Cd is a non-magnetic atom) crystallize in the high-symmetry cubic CsCl - type of structure (space group Pm-3m), which favors the experimental magnetic hyperfine interaction investigation due to the absence of electric quadrupole interactions¹¹ as well as reduces the time for first-principles calculations.

Furthermore, those compounds are great candidates for the B_{hf} successful theoretical outcomes since have single and simple ferromagnetic structure. In addition, since cadmium is diamagnetic, the only contribution to B_{hf} at Cd nucleus comes from the core polarization of the transferred field from the rare-earth host and, consequently, the major B_{hf} component is yielded from s electrons spin - called Fermi Contact contribution. It is known that there is a shortcoming in the electronic band structure codes for B_{hf} calculations.¹⁴ Nevertheless, they are state-of-the-art of *ab initio* calculation in solids and the Fermi Contact contribution has evaluated better than the orbital contribution to B_{hf} .¹⁵ The total hyperfine magnetic field is given by

$$B_{hf} = B_c + B_{orb} + B_{sp}, \quad (1)$$

where B_c is the Fermi contact term, B_{orb} is the field associated with the on-site orbital moment and B_{sp} is the dipolar field from the on-site spin density.

II. FIRST-PRINCIPLES CALCULATIONS

In order to investigate the hyperfine interactions in the RCd series, the theoretical spin band structure calculations based on the DFT formalism have been performed with the full potential linearized augmented plane wave (FP-LAPW)¹⁶ plus local orbitals, as implemented in the ELK code. In the context of the many-body systems under Bloch periodic boundary conditions, the aim of DFT calculations is to predict the ground-state energy whereby functionals of the electronic density. Hence, the problem is solved by finding the spin electron density that minimizes the total energy which, according to Hohenberg and Kohn⁹ is given by

$$E[\rho] = T_s[\rho] + E_{ei}[\rho] + E_H[\rho] + E_{ii}[\rho] + E_{xc}[\rho], \quad (2)$$

where, ρ is the the electronic density (for spin polarized calculations $[\rho] \rightarrow [\rho_\uparrow, \rho_\downarrow]$), $T_s[\rho]$ is the single particle kinetic energy, $E_{ei}[\rho]$ correspond to the Coulomb interaction between electrons and nuclei, the $E_{ii}[\rho]$ term express the interaction between nuclei, $E_H[\rho]$ is the Hartree component of the electron-electron interaction and $E_{xc}[\rho]$ represents the exchange and correlation effects whose were treated using the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE96) parametrization.¹⁷ The computational details are now summarized.

The radius of the non overlapping muffin-tin spheres centered in the atomic positions were 2.8 and 2.6 a.u. for the rare-earth and Cd specimens, respectively. The optimized FP-LAPW parameters are: (i) $K_{max} = 8/R_{MT}^{Cd}$, where K_{max} is the biggest modulus of the

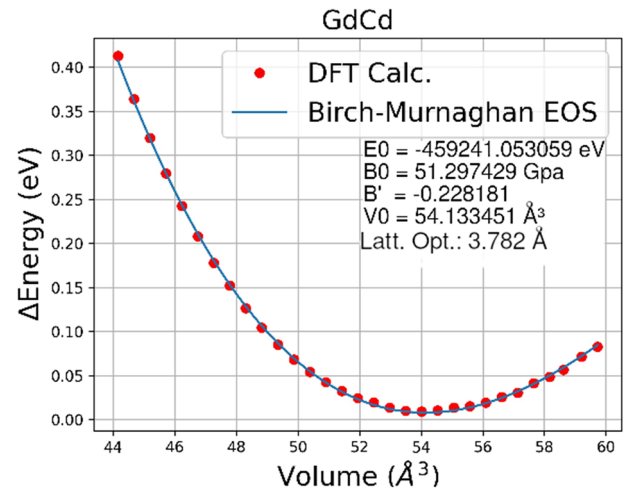


FIG. 1. Variation of DFT total energy for GdCd versus volume (circles) and a cubic fit to the data (solid line).

cutoff wave vector of the plane wave basis in the interstitial region and R_{MT}^{Cd} is cadmium muffin-tin radius; (ii) The mesh of k -points in the irreducible Brillouin zone of the RCd series was set to $15 \times 15 \times 15$. Once the majority RCd elements has ferromagnetic order at low temperatures,^{18,19} ferromagnetic structure and, as a consequence, 2-atoms single cell (one R and one Cd) have been took into account. The crystallographic informations for modeling the RCd unit cells was obtained in the experimental work of Buschow.¹⁸ We have considered the fully optimized RCd equilibrium structures, whose optimization data were fitted using the Birch-Murnaghan equation of state (EOS) given by²⁰

$$E(\eta) = E_0 + \frac{9B_0V_0}{16}(\eta^2 - 1)^2(6 + B'_0(\eta^2 - 1) - 4\eta^2), \quad (3)$$

where the V_0 (volume at zero pressure), B_0 (bulk modulus at zero pressure), B'_0 (pressure derivative) and E_0 (total energy at zero pressure) are fitting parameters and $\eta = (V/V_0)^{1/3}$.

For a case study considering the GdCd system, according to inset image of Fig. 1, the lattice parameter equilibrium predicted by FP-LAPW is about 1.37% greater than the experimental value previously reported by Buschow.¹⁸ This difference for all RCd series is in the range of 1-2% with respect to experimental lattice parameter. Regarding the computed values of V_0 , B_0 and B'_0 , we can observe that they are within the expected range of those predicted by DFT calculations.^{21,22} It is worthwhile mention that the influence of the spin-orbit coupling in our optimization process it was irrelevant.

III. RESULTS AND DISCUSSION

Results of the magnetic hyperfine field for the whole RCd series calculated by ELK code (B_{hf}^{ELK}) taking into account the spin-orbit coupling are displayed in Table I. These magnetic hyperfine fields are compared with those calculated by WIEN2k (B_{hf}^{W2k}) and the experimental data (B_{hf}^{EXP}), both extracted from Cavalcante *et al.*¹¹ As can be

TABLE I. Theoretical values of the total magnetic hyperfine field in Cd position determined by first-principles calculations using ELK code (B_{hf}^{ELK}) and compared with values calculated by WIEN2k (B_{hf}^{W2k}) and experimental values ($B_{hf}^{EXP}(0)$) taken from Ref. 11. The sign of the experimentally determined B_{hf}^{EXP} is unknown.

Compound	Theoretical results		
	B_{hf}^{ELK} (T)	B_{hf}^{W2k} (T)	$B_{hf}^{EXP}(0)$ (T)
CeCd	-6.94	-5.75	5.10
PrCd	-14.51	-13.92	-
NdCd	-21.27	-15.89	17.4
PmCd	-24.28	-	-
SmCd	-22.93	-21.98	21.1
EuCd	-28.51	-	-
GdCd	-38.15	-35.11	30.8
TbCd	-26.40	-25.67	25.6
DyCd	-20.03	-17.91	20.0
HoCd I	-12.64	-11.74	10.3
HoCd II	-12.64	-11.74	11.1
ErCd	-7.06	-6.22	6.9
TmCd	-2.76	-	-
YbCd	-0.83	-	-

seen, we obtained a good hyperfine field prediction for all the RCd series. It is important to mention that for CeCd, considering only spin-orbit coupling in the calculations, the difference was about 63% higher when compared with B_{hf}^{EXP} . This discrepancy is attributed to the high degree of hybridization between the $4f$ and $5d$ electrons as shown in the partial density of states (PDOS) (Fig. 2). To take into account this effect, the on-site correlation through the Hubbard parameter U was used in our calculation for CeCd and the result of $B_{hf}^{ELK} = -6.94$ T is now compatible to the experimental value of $B_{hf}^{EXP} = -5.10$ T. For this calculation, the values of $U = 0.6$ eV and $J = 0$, as reported by Mestnik-Filho *et al.*²³ This is verified in the work of Cavalcante *et al.*,²⁴ where the Hubbard model describes correctly the effect of strong correlations of the $4f$ electrons in the rare-earth elements, leading to a considerable improvement of the agreement between theoretical and experimental hyperfine fields.

The PDOS for CeCd, DyCd, and ErCd (see Fig. 2) reveals that the $4f$ band for Dy and Er are almost isolated from the $5d$ band whereas in CeCd there is a hybridization between them (-0.5 Ha to 0.1 Ha) indicating a stronger correlation, reinforcing the necessity of taking into account the U parameter in the calculations. These predictions suggest that the polarization mechanism may be different in CeCd as compared with DyCd and ErCd. Compounds with rare-earth atoms from Gd to Yb may have the same mechanism where the $4f$ spins couple indirectly through the polarization of conduction s -electrons (f - s coupling). On the other hand, in CeCd and possibly in the compounds with Pr, Nd, Pm, and Sm the coupling occurs between f and $\{d\}$ electrons (f - d coupling). The magnetic measurements¹⁸ performed on polycrystalline RCd materials, reveals different coupling mechanisms in light (Ce, Pr, Nd, Pm, Sm) and heavy (Gd, Tb, Dy, Ho, Er) rare-earth compounds. Buschow considered that the so-called RKKY interaction is responsible for

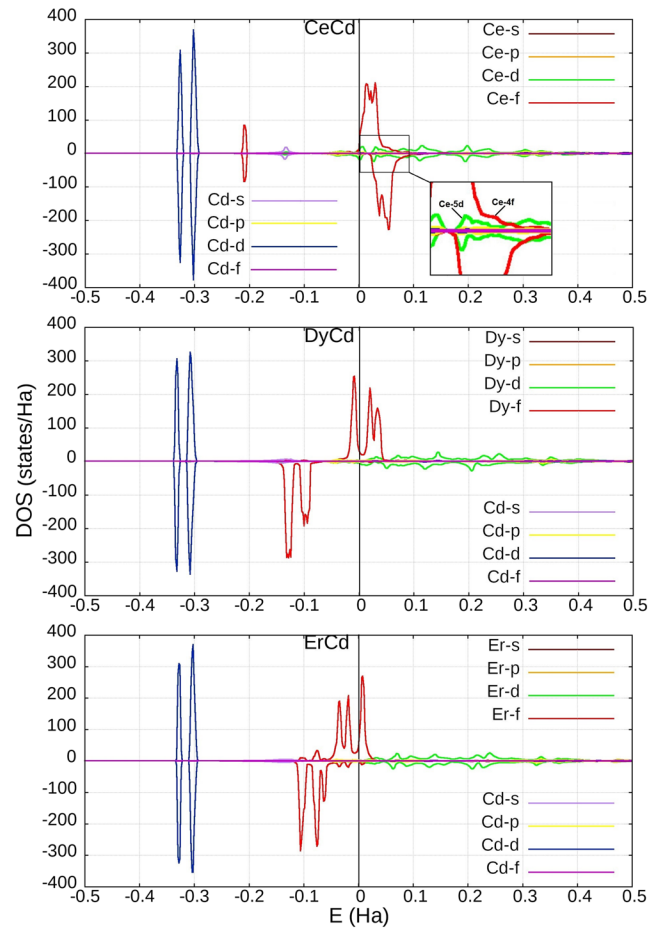


FIG. 2. Partial density of states (PDOS) of CeCd, DyCd, and ErCd relative to Fermi energy ($E = 0$).

the coupling between the heavy rare-earth spins in which the conduction s -electrons are polarized by the $4f$ electrons acquiring an oscillatory character.¹⁸

The Fig. 3 shows the values of the B_{hf} calculated in this work via ELK code compared with those reported by Cavalcante *et al.*¹¹ There is agreement between experimental and our theoretical results with both following a linear dependence on the spin projection $(g - 1)J$ on the total angular momentum J of the rare-earth element. The calculated ELK values are slightly greater than the TDPAC experimental results and WIEN2k values for almost the whole series. This small difference is probably due to the exchange and correlation approximation which is the GGA for ELK calculations whereas the WIEN2k calculations used the local density approximation (LDA)¹¹ as well as some difference in the local base set of plane waves. Moreover, we believe that the use of U parameter could improve the results. For CeCd the calculations of GGA+ U have improved the value of B_{hf} from -13.68 T for spin-orbit coupling to -6.94 T. It is noteworthy, nonetheless, that a faster and easier to use code could provide almost the same results for the B_{hf} than a complex and

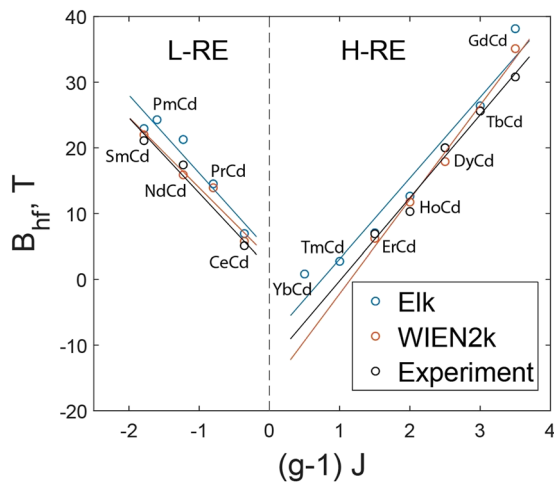


FIG. 3. Spin dependence of experimental (Ref. 11) and theoretical values, calculated by ELK code (this work) and by WIEN2k code (Ref. 11). The experimental values are the saturation values of B_{hf} at 0 K. Straight lines are the linear fit to the values.

time-consuming calculation. In addition, we predict the B_{hf} for PmCd, EuCd, TmCd, and YbCd completing the whole rare-earth series of RCd compounds.

IV. SUMMARY

We perform DFT calculations for the RCd series to investigate the behavior of the magnetic hyperfine interactions at Cd sites and the reliability of the FP-LAPW code ELK. The first-principles calculations were carried out with spin polarization and spin orbit coupling. Calculations for CeCd were also performed by taking the Hubbard parameter into account. Results of density of states shows that the spin transfer mechanism for CeCd and probably for the rest of light rare-earth (Pr, Nd, Pm, Sm) compounds may occur through polarization of d electrons whereas for heavy rare-earth (from Gd to Yb) it is realized by the polarization of conduction s -electrons. The values of the B_{hf} at Cd nuclei for the whole series of RCd were calculated by the ELK code. Even those compounds not experimentally measured such as PrCd, PmCd, EuCd, TmCd, and YbCd follow the linear dependence with the spin projection $(g - 1)J$. The values of B_{hf} are a little higher than the experimental ones, which can be improved by performing calculations adding the U parameter, in order to taking into account the local correlation from RE 4f electrons as demonstrated in the case of CeCd. The high correlation was observed experimentally in the case of RAg where 4f electrons shown anomalous behavior that was attributed by hybridization between 4f-5d electrons.²⁴ Our work revealed that the ELK version used is a good tool in order to determine the hyperfine field in magnetic systems with localized magnetic moments and weak electronic hybridization.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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