An overview of the first principles studies of doped RE-TM5 systems for the development of hard magnetic properties

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Abstract
In this study, we compiled all the first principles calculations performed on RE-TM5 (RE: rare earth, TM: transition metal) system to address the following question: Has everything been tried to improve the hard magnetic properties of this special intermetallic compound, and are there any venues that are worth pursuing? As it is the case with the first principles studies in any field, they are driven mainly by experimental work: (i) to validate their results, and (ii) to extend our understanding of the underlying physical phenomena so that the theory in hand can be used as a predictive tool to shed light on certain what-if scenarios. Our analysis indicates that three major compounds are investigated more than others: (1) YCo5, because it can potentially be an intermediate-performance hard magnet, and the presence of yttrium with no localized 4f electrons simplifies calculations significantly, (2) SmCo5, because it has the largest magnetic anisotropy energy among all RE hard magnets as well as very impressive high temperature performance, (3) CeCo5, because Ce is the most abundant rare earth element with a curious 4f electron behavior that gives rise to pronounced deviations in its structural and magnetic properties across the lanthanides series. This is followed by a brief analysis of several ab initio approaches that were developed to treat these rather complicated systems both at 0 K and at finite temperatures. Towards the end, we elucidate the role of exchange-correlation approximations such as local density approximations (LDA) and generalized gradient approximation (GGA) formulation in determining the MAE and Ms by analyzing their corresponding density of states (DOS), and providing our results on a rather overlooked hard-magnetic material: LaCo5.

Disciplines
Materials Science and Engineering

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In this study, we compiled all the first principles calculations performed on RE-TM$_5$ (RE: rare earth, TM: transition metal) system to address the following question: Has everything been tried to improve the hard magnetic properties of this special intermetallic compound, and are there any venues that are worth pursuing? As it is the case with the first principles studies in any field, they are driven mainly by experimental work: (i) to validate their results, and (ii) to extend our understanding of the underlying physical phenomena so that the theory in hand can be used as a predictive tool to shed light on certain what-if scenarios. Our analysis indicates that three major compounds are investigated more than others: (1) YCo$_5$, because it can potentially be an intermediate-performance hard magnet, and the presence of yttrium with no localized 4f electrons simplifies calculations significantly, (2) SmCo$_5$, because it has the largest magnetic anisotropy energy among all RE hard magnets as well as very impressive high temperature performance, (3) CeCo$_5$, because Ce is the most abundant rare earth element with a curious 4f electron behavior that gives rise to pronounced deviations in its structural and magnetic properties across the lanthanides series. This is followed by a brief analysis of several ab initio approaches that were developed to treat these rather complicated systems both at 0 K and at finite temperatures. Towards the end, we elucidate the role of exchange correlation approximations such as local spin density approximations (LSDA) and generalized gradient approximation (GGA) formulation in determining the MAE and $M_s$ by analyzing their corresponding density of states (DOS) by providing our results on a rather overlooked hard-magnetic material: LaCo$_5$.

1. Introduction:

Permanent magnets have been the “movers and shakers” of the modern technology as they are the key components of traction motors, loudspeakers, wind turbines and several other mass market consumer goods. Their vital role has been the main driving force for the research and development efforts in the last 60 years with a goal of making them lighter, more energy efficient and cheaper. The fundamental properties that are of interest in permanent magnet materials are the Curie temperature, $T_C$, magnetic anisotropy, $K$, and saturation magnetization, $M_s$. $T_C$ is the temperature at which ferromagnetism is lost. In the mean-field approximation, $T_C$ is estimated to be proportional to the magnetic exchange interactions between adjacent spins [1]. In rare earth based hard magnets such as SmCo$_5$, $T_C$ is mainly the result of the exchange interactions between
transition metals as it is much larger than those between rare earth elements. $K$ represents the energy per unit volume required for changing the orientation of the magnetic moments under the application of a magnetic field which is essential for achieving high coercivity in permanent magnets. Magnetic anisotropy can be a result of shape and/or crystalline nature. While shape anisotropy is the main reason that AlNiCo type magnets have their hard magnetic properties [2], it cannot provide a substantial improvement in the anisotropy of a magnet [3]. The second kind is the magnetocrystalline anisotropy energy (MAE) which is intrinsic to a material i.e., insensitive to changes in the microstructure. It is the result of spin-orbit (SO) coupling and its interaction with the crystal electric field (CEF) created by the surrounding charges which produces an energetically favored alignment of magnetic moments along a specific crystalline direction. This second source of anisotropy has potential for further improvement upon doping and inducing slight changes in the lattice parameters. Saturation magnetization, $M_s$, is the magnetic moment per unit volume which is a result of both spin and orbital motion of electrons in a magnetic material. $M_s$ is particularly important when one considers that the maximum energy product, $(BH)_{max}$ is roughly proportional to the square of the $M_s$, $(BH)_{max} \approx M_s^2$ [4].

The main reason we are interested in RE-TM$_5$ system is because of its crystal structure and how it creates a unique TM network to favor a large MAE value. The structure of RE-TM$_5$ is that of a CaCu$_5$ as the prototype (P6/mmm, No.191). This structure can be described as alternating layers of hexagonal nets formed by the TM atoms (2c) with the RE sitting at the center of the net, and planes of TM atoms (3g) arranged in a Kagome network as shown in Fig. 1.

![Fig.1: Crystal structure of RETM$_5$. Ball-and-stick model of the hexagonal unit cell of SmCo$_5$, showing face sharing connected double tetrahedral units; (b) projection into the (001) plane; (c) $z = 0.5$ TM Kagome net; (d) RE and TM atoms in the $z = 0$ (001) plane.](image)

The favorable arrangement of this TM$_5$ network is possibly driving the formation of a large orbital magnetic moment of TM atoms that couples with the spin moment via SO coupling which leads
to large MAE and $M_s$ values [5-7]. This was proven by first principles studies that compare the MAE value of YCo$_5$ with a hypothetical compound Co$_5$ having the same CaCu$_5$ structure with yttrium replaced by a vacancy. It was found that the MAE of Co$_5$ per Co atom is comparable to that of YCo$_5$ proving that MAE is mainly fueled by the special Co$_5$ network in this structure [8]. What is more interesting is that, when the vacant yttrium sites are occupied by an additional cobalt atom producing the Co$_6$ compound, there is a substantial drop in the MAE value which indicates that the itinerant electrons at the RE site distort the CEF responsible for large MAE values [5]. While SO interactions couple the orbital and spin components of magnetic moments, a strong CEF pins the aspherical 4f electron cloud at the RE site according to the crystal lattice giving rise to large MAE values in these compounds [9]. These results underpin an important feature of the RE-TM$_5$ crystal structure: the special arrangement of TM$_5$ network decorated with a RE atom with few itinerant electrons appears to be the fundamental building bricks or “motifs” that gives rise to extraordinary hard magnetic properties.

2. Literature Survey

In this section, we report what has been done in the past, from a first principles approach perspective, to improve the hard-magnetic properties of RE-TM$_5$ compounds. The efforts can be summarized as doping the TM site with impurities such as Fe, Ni, Cu etc., as well as distorting the structural parameters of the unit cell. Both efforts are geared towards manipulating the density of states (DOS) of electrons at the Fermi level with the hopes of improvements in the areas of: (i) MAE due to changes in the SO coupling or crystal field coefficients that gives rise to large anisotropy, (ii) $T_C$ due to enhanced exchange interactions between the TM atoms, (iii) $M_s$ due to enhanced net spin and orbital polarizations.

Our focus will be on three members of the CaCu$_5$ structure i.e., YCo$_5$, CeCo$_5$, SmCo$_5$ mainly because these are the most promising hard magnetic compounds, but they have also been investigated thoroughly by first principles calculations.

2.1. YCo$_5$

There are two main reasons for YCo$_5$ being an active research area. First, it has respectable hard magnetic properties such as a MAE of 6.03 MJ/m$^3$ [10] at room temperature which is comparable to the premiere hard magnetic compound SmCo$_5$ with 17.2 MJ/m$^3$ [11]. This large MAE of YCo$_5$ is mainly because of the orbital polarization of cobalt atoms as mentioned above. In YCo$_5$, research efforts have been centered around doping the specific cobalt sites with other TM atoms to make it a potential intermediate-performance permanent magnet [12]. Secondly, because yttrium lacks 4f electrons, complications originating from the treatment of these localized electrons are absent in this compound; making it an ideal reference material to all the isostructural RE-TM$_5$ compounds [13]. This also allows for identifying the TM network contribution to the overall MAE, $M_s$ and $T_C$ [14].
Important results gathered from the literature on YCo$_5$ system are tabulated in Table 1. Three important figures of merit are provided where data is available, i.e. MAE, $M_s$ and $T_c$. If pure YCo$_5$ is studied only, corresponding data with the density functional theory (DFT) method used is indicated. If the influence of doping is explored, both the doped and the base YCo$_5$ compound values from the same study are reported to discern trends better. To guide the reader, we separate results from different studies with a horizontal line in each table.

Based on the compilation of data in Table 1, magnetic moments seem to agree well irrespective of the DFT formalisms used. However, MAE values differ substantially. One reason for the large scatter in data is because MAE values are only a few meV per formula unit which requires very accurate calculations with strict convergence criteria. More importantly, because the MAE in YCo$_5$ originates mainly from the orbital moment of Co atoms, the SO coupling effects in TM are poorly described even by the state-of-the-art first principles approaches; thus, giving rise to incorrect MAE values [15]. While we delay an elaborate treatment of these various DFT calculations until the next section, it is worth mentioning that generalized gradient approximation (GGA) methods for exchange and correlation effects with an on-site Coulomb interaction parameter $U$ seems to capture the physics of this system slightly better than others.

As for the doping efforts in YCo$_5$, mainly Fe, Ni and Cu are used to occupy a fraction of Co sites in hopes of modifying the 3d electronic density of states and improving the hard magnetic properties of the system. The main influence of the additions of these atoms on the 3d states of Co is the electron doping in the case of Ni and Cu, and hole doping in the case of Fe that shifts the fermi level. Studies involving Fe have found that the magnetic moment per unit cell increases
with Fe doping showing a Slater-Pauling relationship in these alloys, while MAE in general decreases [5,19,20,24]. Although, in some other studies, the MAE has been calculated to increase upon trace amount doping with Fe [23] as well as when it is co-doped with Cu [14]. Ni is seldom used to modify the electronic structure in this system, except one study in which they found a reduction of both the magnetic moment and T_C [19].

2.1. SmCo_5

SmCo_5 has the largest known uniaxial MAE of 17.2 MJ/m^3 [11]. Because a substantial fraction of this compound is rare-earth ≈17 at%, it was thought that structures derived from this system with more TM content such as Sm_2Co_17 would provide larger magnetic inductions; hence, larger energy products. However, unfortunately other compounds derived from the SmCo_5 family do not possess as large MAE values [25]. This is why, research efforts in this area have been to substitute either the samarium or the cobalt sites with small additions of impurities without distorting the crystal structure.

Large uniaxial MAE in SmCo_5 stems mainly from two things: (i) SO coupling of localized and partially filled 4f electrons of samarium, and (ii) SO coupling of the itinerant 3d electrons of cobalt within a strong CEF [20]. High Curie temperature (T_C ≈1020), on the other hand, is mainly the result of strong interatomic exchange coupling of cobalt atoms as the small de Gennes factor of Sm makes its contribution negligible [26]. While SmCo_5 is a very attractive hard magnet from the standpoint of MAE and T_C values, limited saturation magnetization, M_s, values is where researchers run into bottlenecks. Low M_s results in low energy product, (BH)_max of 231 kJ/m^3 for SmCo_5 that is nearly half the value of the champion permanent magnet Nd_2Fe_14B with, (BH)_max of 512 kJ/m^3 [11,27], hence making up only ≈3% of the total permanent magnet production market [28].
Similar to YCo$_5$, magnetic moment calculations of SmCo$_5$ from various DFT methods agree with experiment favorably. However, MAE values suffer a large degree of variation due to: (i) inadequacy of the \textit{ab initio} methods to correctly describe the electronic structure of localized 4f electrons as well as (ii) underestimation of the orbital component of magnetization in 3d electrons of TM atoms. This is why, comparative analysis of MAE values should be done within a study to understand trends, and not across different groups which would lead to misleading interpretation of data.

While main substitutional impurities for the cobalt site seems to be iron and nickel; for samarium sites it is cerium. These dopants are preferred mainly because they are more abundant in the Earth’s crust [35] which makes them ideal candidates to reduce the dependence on critical elements. In addition to providing reduced criticality, Fe also improves the magnetic moment as shown in multiple studies [23,30,32]. The enhancement of magnetic moment would have been maximized had SmFe$_5$ been stable, but thermodynamics dictate that 1:5 structure does not form with iron [30]. This is linked to the reduced number 3d electrons upon doping with iron which can be compensated and stabilized by doping it with 3d electron rich nickel [30,36]. The extended stability of this hexagonal structure through additions of nickel comes at the price of reduced magnetic moment and MAE. Nevertheless, the energy product of SmCo$_2$NiFe$_2$ is speculated to be nearly 361 kJ/m$^3$ which is 56 % larger than that of SmCo$_5$; thus, making it an ideal intermediate performance magnet [36].

Besides doping with impurities, straining the c-axis was shown to manipulate the electronic structure and magnetic properties of SmCo$_5$. Elongating the c-axis while keeping the volume
constant results in reduced magnetic moment due to reduced interplanar overlap of the 3d electrons. However, MAE increased by about 30% upon straining the lattice due to the redistribution of electrons across various m states which enhances the orbital contribution to MAE [34].

2.3. CeCo5

The fact that cerium is the most abundant rare earth element makes CeCo5 a particularly attractive compound despite its modest hard magnetic properties [35]. In addition, what makes CeCo5 interesting from a first principles standpoint is that, cerium has only one 4f electron that is argued to have an itinerant character which brings about a fractional occupation of the 4f states rather than being one [37,38]. The hybridization between the itinerant 4f-3d electrons was shown to be the underlying reason for the anomalous drop in the lattice parameter, TC, and the magnetic moment of CeCo5 across the lanthanide series [13]. Specifically, the structural and magnetic properties of CeCo5 does not follow LaCo5 and PrCo5 series in a linear fashion. This discrepancy is mainly ascribed to the additional bonding between Ce-4f and Co-3d electrons creating mixed valency, i.e., Ce3+ and Ce4+, as bonding weakens magnetism which is a well-known property of itinerany ferromagnetism [39]. In particular, the evidence of this unexpected behavior of 4f electrons was that the ground state properties and the aforementioned deviations in structural and magnetic properties were described better with first principles calculations when these electrons are treated as itinerant and not localized unlike the rest of the lanthanide series. In particular, it was shown through DOS calculations that the spectral weight of Co at the fermi level is reduced due to the interactions between the 4f electrons of Ce; hence, the drop in the overall magnetization [13].

The hybridization problem that gives rise to reduced hard magnetic properties were partially cured by doping some of the cobalt sites with copper which favors the Ce3+ state over Ce4+ as the cerium in CeCu5 is found to be in the Ce3+ state [40]. Copper impurities in the lattice are believed to create an asymmetric charge distribution along the uniaxial direction that enhances the MAE as well as pushing the 4f electrons to the cerium sites. However, the enhanced MAE is accompanied by reduced magnetization mainly because Cu is non-magnetic which means small additions of Cu will be ideal to optimize its performance.
In addition to YCo$_5$, SmCo$_5$ and CeCo$_5$ compounds, GdCo$_5$ is explored with ab initio techniques because it has a symmetric 4f shell giving rise to a net zero orbital magnetization which lifts the complications due to interactions with the CEF. In addition, its magnetization increases with temperature due to Gd moments disordering more rapidly than Co in the lattice. The opposing Gd and Co moments also give rise to a compensation temperature at which the net magnetization is zero [43]. NdCo$_5$ has large magnetization, but the in-plane anisotropy of this compound is well known and proven both experimentally and theoretically [44,45]. Heavy rare earth 1:5 compounds such as DyCo$_5$ and TbCo$_5$ were studied mainly to elucidate the role of on-site Coulomb interaction parameter, U, in finding the true magnetic ground state of each system [46].

In one study, RE elements are replaced by heavy 4d and 5d TM elements to explore the possibility of obtaining hard magnetic properties [47]. Although compounds such as YFe$_5$, ZrFe$_5$, HfFe$_5$, ZrCo$_5$, and HfCo$_5$ are shown to be thermodynamically stable based on the heat of formation results, none has promising magnetic properties that could match their rare-earth based 1:5 counterparts.

3. First Principles Methods

3.1. 0 K

First principles calculations using Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) to approximate the exchange and correlation effects within the DFT have
been very successful in calculating the electronic structure of materials in the last two decades. The theory works especially well with materials in which the valence electron structure is dominated mainly by s or p orbitals owing to the fact that these electrons experience an average potential, consistent with the LDA/GGA approximations. However, materials in which the valence electron structure is of d or f orbital character, these approximations fail to describe their electronic structure dictated properties, i.e., crystal structure, optical and magnetic properties. The main reason for this discrepancy is that while LDA/GGA approximations assume that every electron is in the same average potential bath, electrons occupying the localized d or f orbitals are under the influence of some additional non-local interaction due to the neighboring localized dynamic electrons [48]. This makes it an intractable multi-body problem which is hard to approximate with the LDA/GGA schemes.

Applying LDA/GGA techniques, without any corrections, to well-known hard magnets with f electrons such as SmCo$_5$ or even magnets with only d electrons – transition metals – results in inaccurate magnetic moment and MAE calculations [8,49,50]. This deviation is tied to incorrectly pinning the f electrons at the Fermi level while, in reality, occupied (unoccupied) electrons are pushed down (up) in energy due to strong correlation effects in these localized states [3]. Because the correlations effects, i.e., strong electron-electron interactions, cause band narrowing which drives the local moment formation, inclusions of these effects in the LDA/GGA schemes will improve the accuracy of calculations resulting in more realistic values for the MAE, orbital magnetic moments etc. [15].

To improve the accuracy of the Density Functional Theory (DFT) formalisms, several corrections were applied that can be conceived as rather empirical with parameters that have no rigorous definition in condensed matter physics [8]. First is the introduction of a Hubbard U parameter within the LDA scheme which entails the addition of on-site Coulomb U and exchange J corrections on top of the LDA energy [51,52]. These corrections are added to push down (up) the occupied (unoccupied) f electron states, reflective of the scenario described above. The success of the so called LDA/GGA +U method is shown in several calculations conducted on strongly correlated systems [32, 53,54]. In one study, this correction is successfully applied on both YCo$_5$ and LaCo$_5$ that made the authors claim the existence of a universal set of U-J parameters that can be confidently used on RECo$_5$ structures [21]. However, it is worth mentioning that both yttrium and lanthanum have empty 4f spin up/down subshells making them free from complications associated with this strongly localized orbital. Other approaches like the “open core” scheme freezes the 4f electrons in the core and treats them within the Hubbard I approximation (HIA) [55,56] in charge-self consistent dynamical mean field theory (DMFT) [33]. This method captures the main physics of electronic structure in materials that are strongly correlated, i.e., SmCo$_5$ and gives magnetic moment values that are only 10% lower than experimental data [33]. However, it is computationally demanding which makes MAE calculations very impractical. To facilitate such calculations, an extension of DMFT-HIA is introduced as standard rare-earth model (SRM) [57,58] which still treats 4f electrons as core electrons, but does not allow any hybridization with other valence electrons. The third approach is the inclusion of a local self-interaction correction (LSIC) to the f states [59]. In LSIC, much as the on-site Coulomb U interaction parameter described above, self-interaction correction terms are
added to localize the 4f states which allows the self-exchange energies to be accurately calculated [18].

As for the 3d electrons of TMs, orbital polarization (OP) corrections are added to unquench the orbital moments which is essential not only for accurate moment calculations, but also for obtaining reliable MAE values as the magnitude of orbital moments are particularly important in determining magnetic anisotropy [30, 60]. OP scheme originates from the on-site electron interactions between d electrons which prevents double occupancy in the d orbitals; hence, giving rise to local orbital moment formation [61].

3.2. Finite Temperatures

Ground state properties extracted from a DFT calculation at 0 K are very essential in understanding the trends in magnetic properties across the lanthanide series. However, they provide no information on the temperature dependence of these properties. Therefore, being able to extrapolate first principles calculations to finite temperatures is crucial, mainly because these magnets will operate in demanding environments where high temperature performance is critical. Unfortunately, there is no – strictly speaking – robust first principles methods that embody the finite temperature properties of these RE-TM intermetallics. The absence of such a methodology is linked to the complex and dynamic interplay between the 3d electrons of TMs and 4f electrons of RE elements as the temperature is varied. Namely, in RE-TM magnets, while 4f electrons are mainly responsible for low temperature magnetism, high temperature magnetism is predominantly governed by 3d electrons of TMs [62]. This means, to accurately describe the thermomagnetic properties – MAE (T), T_C, and M(T) – of RE-TM magnets, theoretical treatments of the temperature dependence of 3d electronic states need to be very robust.

To address the finite temperature magnetism problem in RE-TM magnets, a few schemes have been developed with disordered lattice model (DLM) being the most applicable one for the study of permanent magnets. In this model, spin-spin correlations give rise to local moments which point in various orientations with a resultant potential energy that describes the canonical features of this ensemble. Temperature fluctuations of these local moments are described with classical mechanics and their distribution given by Boltzmann statistics [18]. In addition, thermal disorder is incorporated into the model using the Coherent Potential Approximation (CPA) which was developed to treat impurities in alloys [63]. CPA simplifies the model by averaging over random potentials and treating the microstates as if they are in a uniform potential. According to this model, T_C is the minimum temperature at which all the local moments result in a net zero polarization; thus, resulting in a paramagnetic state. Within DFT-DLM, T_C is obtained through calculations of Weiss fields self-consistently using the average potential from the CPA, and determining the temperature at which these fields vanish by Monte Carlo integration or other mean field approximations [64].

Thanks to the inclusion of (SO) coupling for the 3d and 4f electrons within the DFT-DLM approach, temperature dependent MAE of L1_0 FePt [65, 66] and of YCo5 [17] were described with impressive
success, mainly because in both magnetic materials, electronic structure is dictated by 3d electrons only. However, one weakness of the DLM approach is that the potentials are approximated to be spherical at the RE site which renders the MAE(T) calculations useless as it is well known that 4f electron shell is aspherical [67]. One solution that is proposed to tackle this problem is to replace all RE sites in RE-TM compounds by yttrium which is 4f electron free; hence, removing complications associated with it [68]. Obviously, although the absolute values of calculated MAE and crystal field coefficients are irrelevant, and have no meaning in this treatment, it is still worthwhile to understand trends across various materials.

Other techniques to calculate $T_C$ of magnetic materials rely on estimating the exchange interaction parameter from the energy difference between ferromagnetic and antiferromagnetic spin configurations. These intrinsic parameters from the DFT calculations are used to calculate the $T_C$ either by mean field approaches assuming a Heisenberg model, or by a Monte Carlo integration [64,69].

4. A Case Study: LaCo$_5$

In this section, we want to show the importance of the exchange correlation parameters in solving the one-particle Schrödinger equation, the Kohn-Sham equation, and how it impacts the critical magnetic properties by providing our results on a rather overlooked hard-magnetic material: LaCo$_5$. This compound has lanthanum at the RE sites with no 4f electrons. However, it still has respectable MAE of $\approx 5 \text{ meV/fu}$ [21] due to the special cobalt network. We provide our atomic site resolved contributions to magnetic properties of LaCo$_5$ in Table 1 which we also compare it with an earlier study. The calculations were carried out with the WIEN2k code, a full potential, linearized augmented plane wave DFT method [70]. The k-space integrations have been performed at least with $15 \times 15 \times 17$ Brillouin zone mesh which was sufficient for the convergence of total energies ($10^{-6}$ Ryd.), charges, and magnetic moments. For RCo$_5$ systems, the higher values of plane-wave cut-off ($R_{\text{Kmax.}} = 9.0$ and $G_{\text{max.}} = 14$) are required. Here, MAE is calculated using the force method, where difference was taken between c-axis and the planar of the total eigenvalue energies for both spins.

$$MAE \approx \sum \text{occupied} \varepsilon_l \tilde{a}_{\text{plane}} - \sum \text{occupied} \varepsilon_l \tilde{a}_{\text{z-axis}}$$

where, $\varepsilon$ is the sum of eigenvalues for both spins in corresponding directions and $\tilde{a}_{\text{z-axis}}$ and $\tilde{a}_{\text{planar}}$ are easy and planar directions. The positive (negative) values for the corresponding MAE correspond to the uniaxial and planar anisotropy.

In our calculations we deployed both local spin density approximations (LSDA) [71] and generalized gradient approximation (GGA) formulation of Perdew, Burke, and Ernzerhof (PBE-1996) [72]. LSDA is formulated to work well in systems in which the electron density varies slowly. GGA method, in some ways, is an improvement to LSDA, in that, it not only considers the electron
density of the atom but also the density in the neighboring sites. We haven’t used a Hubbard U correlation parameter as we do not have strongly correlated f electrons in LaCo$_5$ which is in stark contrast to an earlier study on the same compound [21] as shown in table 1.

<table>
<thead>
<tr>
<th>Atomic Sites</th>
<th>GGA (S/L)</th>
<th>LSDA (S/L)</th>
<th>GGA + U at Co sites (S/L) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interstitial</td>
<td>0.60</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>$La$</td>
<td>-0.186 / 0.0823</td>
<td>-0.153 / 0.007</td>
<td>-0.283 / 0.027</td>
</tr>
<tr>
<td>$Co(2e)$</td>
<td>1.574 / 0.103</td>
<td>1.492 / 0.108</td>
<td>1.628 / 0.152</td>
</tr>
<tr>
<td>$Co(3g1)$</td>
<td>1.556 / 0.085</td>
<td>1.465 / 0.0857</td>
<td>1.663 / 0.139</td>
</tr>
<tr>
<td>$Co(3g2)$</td>
<td>1.557 / 0.119</td>
<td>1.467 / 0.124</td>
<td>1.663 / 0.139</td>
</tr>
<tr>
<td>Total moment</td>
<td>7.431</td>
<td>7.362</td>
<td>8.71</td>
</tr>
<tr>
<td>MAE (meV/fu)</td>
<td>1.41</td>
<td>0.552</td>
<td>4.402</td>
</tr>
</tbody>
</table>

$^a$Ref.[21]

While the magnetic moments do not differ between the GGA and LSDA methods, GGA gives MAE values that are more favorable with the experimental values. We explore this difference by providing the DOS of each crystallographically distinct cobalt site as well as the lanthanum site in figures 5, 6 and 7.
Fig. 5: The PDOS of crystallographically inequivalent Co sites and La site along the [100] direction. Intensity of La sites are amplified 5 times to show hybridization between La and Co.
In figures 6 and 7, the intensity of lanthanum site is amplified 5 times to show the hybridization between the lanthanum and cobalt atoms at the Fermi level, $E_F$. The peaks near the $E_F$ for both lanthanum and cobalt atoms appear at the same energy level indicating their collective contribution to bonding. More importantly, from table 1, it is obvious that the calculated MAE within the GGA method is in far better agreement with experimental value than that of the LSDA approach. This difference can be appreciated by carefully analyzing the DOS along the [100] and [001] directions for the cobalt sites as illustrated in Fig. 7. The shaded regions indicate the DOS for the in-plane [100] axis, whereas the dashed lines indicate the corresponding quantity along the uniaxial [001] direction for both GGA and LSDA. As indicated with arrows, the change in DOS between the [100] and [001] axes within the GGA is more significant than the LSDA method especially for the Co(3g$_2$) site. Because of this difference, MAE value within the GGA is higher and closer to the experimental findings.
5. Conclusions & Outlook

In this review article, we attempted to treat the important RE(TM)$_5$ compound system which is known for its high magnetic anisotropic properties due to its unique arrangement in space. Our analysis comprised mainly of first principles (DFT) approaches rather than experimental results. A few key points that can be extracted from this study are as follows:

i. 1:5 system has a special network of TM atoms which can provide remarkable magnetic anisotropies when the TM sites are occupied atoms with relatively more localized electronic structure such as cobalt.

ii. 1:5 structure is not explored as much as it should have been within the first principles methodologies. Various substitution scenarios at the TM sites such as with iron, nickel, copper; or at the RE site with cerium are explored. These types of exploratory searches should be extended with other impurities such as with alkaline metals as a recent experimental study on paramagnetic CeCo$_3$ finds that magnesium alloying induces a ferromagnetic transition with intrinsic properties large enough for permanent magnet applications [73].
iii. In addition to various impurity substitutions, the effect of interstitial atoms such as nitrogen, hydrogen or carbon on magnetism should be explored as this structure is suitable due to its tetrahedral sites created by TM atoms.

iv. As a final note, DFT provides us with unique capabilities to “perform experiments” in virtual machines which is one of the greatest strengths available to us nowadays. It can certainly guide experiments in a meaningful way. However, the approximations made to treat strongly correlated systems as described in the article should be selected judiciously as it can result in completely unphysical solutions.

References:


