Rare-earth/transition-metal magnets at finite temperature: Self-interaction-corrected relativistic density functional theory in the disordered local moment picture

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Atomic-scale computational modeling of technologically relevant permanent magnetic materials faces two key challenges. First, a material’s magnetic properties depend sensitively on temperature, so the calculations must account for thermally induced magnetic disorder. Second, the most widely used permanent magnets are based on rare-earth elements, whose highly localized 4f electrons are poorly described by standard electronic structure methods. Here, we take two established theories, the disordered local moment picture of thermally induced magnetic disorder and self-interaction-corrected density functional theory, and devise a computational framework to overcome these challenges. Using this approach, we calculate magnetic moments and Curie temperatures of the rare-earth cobalt (RECO5) family for RE = Y-Lu. The calculations correctly reproduce the experimentally measured trends across the series and confirm that, apart from the hypothetical compound EuCo5, SmCo5 has the strongest magnetic properties at high temperature. An order-parameter analysis demonstrates that varying the RE has a surprisingly strong effect on the Co-Co magnetic interactions determining the Curie temperature, even when the lattice parameters are kept fixed. We propose the origin of this behavior is a small contribution to the density from f-character electrons located close to the Fermi level.

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I. INTRODUCTION

In solids, the 15 lanthanides (atomic numbers 57–71) usually exist in a 3+ state, with three electrons (two of s and one of d character) donated to the valence band. Grouping the lanthanides with Y and Sc, which behave in the same way, forms the group of elements known as the “rare earths” (REs) [1]. The chemical variation within the REs originates from their strongly localized 4f spin-up and -down subshells, which vary from being totally empty (Sc/Y/La, 4f0) to totally filled (Lu, 4f14). Lying at the center of the lanthanide block, Gd (4f7) has one completely filled and one completely empty spin subshell, and marks the boundary between the “light” (Sc-Eu) and the “heavy” REs (Gd-Lu). Notable anomalous lanthanides include Ce, whose valence varies due to the relative ease that its single 4f electron can delocalize; Pm, which is radioactively unstable; and Eu and Yb which, rather than having a single hole in a spin subshell associated with the 3+ state, usually prefer to capture an additional 4f electron and adopt a 2+ state [1,2].

Aside from their uses in, e.g., catalysts, batteries, and energy-efficient lighting [3], the excellent magnetic properties of Sm-Co [4] and Nd-Fe-B [5,6] compounds have led to REs becoming critical to many industries as components in high-performance permanent magnets [7]. The key principle underlying such magnets is that while elemental transition metals (TM)s like Fe and Co remain strongly magnetic up to very high temperatures (~1000 K), they are relatively easy to demagnetize with external fields [8]. Alloying the elemental TM s with the REs largely retains their good high-temperature properties while simultaneously providing a massive increase in the coercivity (resistance to demagnetization) [8].

The principal microscopic mechanism driving this increased coercivity is the electrostatic interaction of the localized RE-4f electrons with their environment (the crystal field) [9]. The magnetic moment associated with the RE-4f electrons gains a strong directional preference, i.e., magnetocrystalline anisotropy, which anchors the TM magnetism along the same axis through the RE-TM exchange interaction. The benefits of this alloying approach can be seen in SmCo5, whose Curie temperature (TC) of 1020 K is comparable to pure Co (1360 K) [8,10] but whose magnetocrystalline anisotropy energy density is 20 times larger [11]. Indeed, over 50 years since its discovery the high-temperature properties of SmCo5 remain hard to beat [7].

This simple picture, that the RE provides the coercivity and the TM provides the large magnetization and TC, is an oversimplification since it neglects the contribution to the magnetization from the REs themselves. A more coherent picture of RE-TM intermetallics [9] models the RE as an array of isolated 3+ ions interacting with the crystal field and an effective magnetic field originating from the RE-TM exchange interaction. Diagonalization of the crystal-field Hamiltonian gives the RE contribution to the magnetization and anisotropy. The TM contribution is deduced empirically from RE-TM compounds with a nonmagnetic RE, like Y [12].

The crystal-field picture does an excellent job of explaining the temperature dependence of magnetic quantities which are heavily RE dependent, such as the low-temperature anisotropy and magnetization [9,12]. However, the phenomenological description of the TM limits the predictive power of the theory, especially with regard to TC. Since a material rapidly loses its magnetic properties at temperatures in the vicinity of its Curie temperature, having a high TC is very useful for practical permanent magnets. It is known experimentally
that $T_C$ is RE dependent: referring to the experimental review of Ref. [10], SmCo$_5$ has the highest $T_C$ of the compounds that form stoichiometrically as RECo$_5$ (1020 K), slightly higher than GdCo$_5$ (1014 K). Meanwhile, for the RE$_2$Co$_7$ and RE$_3$Co$_{17}$ series of magnets it is RE = Gd which has the highest $T_C$ (771/1218 K) with RE = Sm lower (713/1195 K). The fact that Gd has the largest spin moment of the REs might suggest some correlation of this quantity with $T_C$, but the RE$_2$Co$_7$ series provides the counterexamples of RE = Dy and Ho, whose nominal spin moments are larger than Sm but whose $T_C$ is smaller (640 and 647 K) [10]. Magnetoostructural effects could also play a role, with the RE modifying the lattice constants and thus the magnetic interactions [13]. However, it is by no means clear how these and other effects might combine to influence $T_C$.

A predictive, first-principles theory of the $T_C$ of RE-TM magnets could provide insight into the physical processes governing the high-temperature performance of these magnets, and suggest strategies for further optimization. However, such a theory is currently missing. Density functional theory (DFT) [14] provides a practical framework to perform first-principles studies of RE-TM magnets, but is faced with the challenge of describing with sufficient accuracy (i) the finite-temperature disorder of the magnetic moments and (ii) the complex interactions between the localized RE-4$f$ electrons and their itinerant counterparts.

In this work, we introduce a theory which attacks these two problems directly. Finite-temperature effects are modeled within the disordered local moment (DLM) [15,16] picture, which is reviewed in Sec. II. Meanwhile, the problematic RE-4$f$ electrons are treated within DFT using the local self-interaction correction (LSIC) [17]. Previous modeling of REs within this framework has been limited to Gd [18–21], but the developments described in Sec. III now allow investigation of the entire RE series for the same computational cost. We use this theory to study the RECo$_5$ family of magnets (Fig. 1), exploring the evolution of magnetism from 0 K (Sec. IV) to $T_C$ (Sec. V). We conclude with our analysis of why, as is observed experimentally, the calculations find SmCo$_5$ to have the highest $T_C$ of the RECo$_5$ magnets (Sec. VI).

II. DFT-DLM APPROACH

At finite temperature, the functional properties of all materials are modified to some extent due to the thermal population of excited vibrational states, e.g., thermal expansion or increased electrical resistivity [22,23]. However, independent of lattice vibrations, the magnetic properties of a material are extremely sensitive to temperature. The disordered local moment (DLM) picture of magnetism provides a conceptual basis to understand this temperature variation [15]. Here, the material is modeled as an array of microscopic magnetic moments (e.g., one associated with each atom), of fixed magnitude but variable orientation. This picture of local moments makes no assumption that the electrons themselves are localized; for example, the 3$d$ electrons responsible for magnetism in Fe, the prototypical DLM metal, are completely itinerant [24]. Rather, the spin-spin correlation between electrons near atomic sites can be strong enough to establish magnetically polarized regions which exist for much longer timescales than those associated with electron motion [15]. These are the local moments.

A DLM magnetic microstate is specified by the orientations $\{\hat{e}_i\} = \{\hat{e}_1, \ldots, \hat{e}_N\}$ of the $N$ local moments. The grand potential energy $\Omega(\{\hat{e}_i\})$ is a function of these local moment orientations, and the (classical) statistical mechanics of the system is determined by the partition function

$$Z = \int d\hat{e}_1 d\hat{e}_2 \ldots d\hat{e}_N \exp \left[ -\beta \Omega(\{\hat{e}_i\}) \right],$$

(1)

where $1/\beta = k_B T$, and $T$ and $k_B$ are the temperature and Boltzmann constant. Experimental measurements correspond to thermal averages over the magnetic microstates. For instance, a magnetization measurement probes the average orientations of the local moments,

$$\langle \hat{e}_j \rangle_T = \frac{1}{Z} \int \hat{e}_j d\hat{e}_1 d\hat{e}_2 \ldots d\hat{e}_N \exp \left[ -\beta \Omega(\{\hat{e}_i\}) \right].$$

(2)

The DLM paramagnetic state corresponds to each orientation averaging to zero, $\langle \hat{e}_j \rangle_T = 0$, and the highest temperature at which $\langle \hat{e}_j \rangle_T \neq 0$ corresponds to the Curie temperature $T_C$.

In principle, DFT provides a pathway to a first-principles DLM theory through the possibility of evaluating the grand potential energy $\Omega(\{\hat{e}_i\})$, although finding a sufficiently accurate approximation for the exact exchange-correlation functional remains an ongoing and formidable challenge [25,26]. Specifically, $\Omega(\{\hat{e}_i\})$ could be obtained from constrained DFT calculations, with the applied constraints forcing the local magnetizations to point along designated local moment directions $\{\hat{e}_i\}$ [15]. In practice however, any direct attempt to perform statistical mechanics would soon be faced with the problem of covering the huge phase space spanned by $\{\hat{e}_i\}$, requiring an effectively infinite supercell to contain all $N$ local moments.

A popular method of circumventing this problem is to replace the "exact" $\Omega$ with a model, e.g., a Heisenberg model based on pairwise interactions between local moments. The model parameters are extracted from DFT calculations, e.g., from the Liechtenstein formula [27] or constrained DFT [28]. $T_C$ is then obtained from the simpler statistical mechanics of the model, which might be solved through a mean field approach, the random-phase approximation, or Monte Carlo integration [29–33].
These schemes require striking a balance between a model which is sufficiently complex to capture the necessary magnetic interactions, yet simple enough for the statistical mechanics problem to be tractable. The most popular pairwise model should, as its name suggests, only apply when the interaction between two local moments is independent of the alignments of all other local moments in the system. This picture is not particularly intuitive in a metal where one would expect a cooperative effect, i.e., magnetic interactions being reinforced when the material is in a global ferromagnetic state and weakened in the paramagnetic state. Practically, this issue leads to the question of whether one should parametrize the pairwise model for the ferromagnetic or paramagnetic state [27], and what to do at intermediate temperatures [34].

The DFT-DLM theory described in [15] approaches the problem in a different way. Instead of approximating the grand potential energy, one instead introduces an auxiliary quantity $\Omega_0(\hat{\epsilon}_i)$ with a known functional form

$$\Omega_0(\hat{\epsilon}_i) = -\sum_i \hat{h}_i \cdot \hat{\epsilon}_i,$$

where the “Weiss fields” $\{\hat{h}_i\}$ are obtained self-consistently. Specifically, the thermodynamic inequality

$$F(T) \leq F_0(T) + \langle \Omega \rangle_{0,T} - \langle \Omega_0 \rangle_{0,T}$$

provides a relation between the exact free energy $F(T)$ and the free energy of the auxiliary system $F_0(T) = -k_B T \ln Z_0$, with

$$Z_0 = \prod_i \int d\epsilon_i \exp[\lambda_i \cdot \hat{\epsilon}_i] = \prod_i \frac{4\pi}{\lambda_i} \sinh \lambda_i,$$

and $\lambda_i = \beta \hat{h}_i$. Crucially, the thermal averages $(\ldots)_{0,T}$ appearing in the inequality (4) are calculated with respect to the auxiliary system, e.g.,

$$\langle \Omega \rangle_{0,T} = \frac{1}{Z_0} \prod_j \int d\epsilon_j \exp[\lambda_j \cdot \hat{\epsilon}_j] \Omega(\hat{\epsilon}_j).$$

The Weiss fields are chosen to minimize the right-hand side of the inequality (4). Then,

$$\hat{h}_i = -\frac{3}{4\pi} \int d\epsilon_i \langle \Omega \rangle_{0,T} \hat{\epsilon}_i (\hat{\epsilon}_i),$$

The partial average $\langle \Omega \rangle_{0,T}$ integrates over all the degrees of freedom in Eq. (6) except the single local moment orientation $\hat{\epsilon}_i$. The Weiss fields have the periodicity of the magnetic unit cell, i.e., the number of distinct Weiss fields equals the number of magnetic sublattices.

As indicated by Eq. (7), the Weiss fields are temperature dependent. The DFT-DLM estimate of $T_C$ is the temperature at which all the Weiss fields vanish. Alternatively, one can introduce local order parameters

$$m_i(T) \equiv \langle \hat{\epsilon}_i \rangle_{0,T} = \hat{\lambda}_i L(\lambda_i),$$

with $L(\lambda_i) = \coth(\lambda_i) - 1/\lambda_i$. These quantities vary between 1 at zero temperature and 0 at $T_C$.

We stress that the key quantities in the DFT-DLM theory, the Weiss fields $\{\hat{h}_i\}$, are calculated with the full grand potential energy $\Omega$, without any assumption on the nature of the underlying interactions, e.g., pairwise, four-spin, etc. [18]. Furthermore, through the averaging in Eq. (7) the magnitudes of the Weiss fields are indeed influenced by the degree of global order in the system, ensuring self-consistency between $\{\hat{h}_i\}$ and the “reference state” used to calculate them.

The partial average $\langle \Omega \rangle_{0,T}$ appearing in Eq. (7) still presents a challenge to the most widely used implementations of DFT, which solve the Kohn-Sham equations to determine single-particle wave functions [14]. However, the Green’s-function-based Korringa-Kohn-Rostoker multiple-scattering formulation of DFT, in combination with the coherent potential approximation (KKR-CPA) [35], allows the partial average to be recast as an impurity problem. This impurity problem, which sees each local moment sitting in an effective medium designed to mimic the averaged properties of the disordered system, can be solved using the same KKR-CPA techniques originally developed to tackle compositional disorder in the simulation of alloys [36]. The DFT-DLM theory has undergone a number of developments from its original formulation, and is being applied to an increasingly wide range of magnetic systems [19–21,37,38]. The practical steps to calculating self-consistent Weiss fields and the key multiple-scattering equations are described in Refs. [16,19,39].

The fact that the DFT-DLM theory is rooted in KKR-CPA has both advantages and disadvantages. Thermally averaged quantities, e.g., spin and orbital moments, can be calculated relatively easily by tracing the relevant operators with the Green’s function. The calculations include both core and valence electrons explicitly, and the structure of the KKR-CPA equations allow for a very high degree of numerical precision, e.g., in evaluating integrals over the the Brillouin zone [40]. However, the formalism generally involves making a shape approximation to the Kohn-Sham potential (here we use the atomic sphere approximation, ASA) which, although allowing a compact angular momentum basis to be used to describe the Green’s function and scattering matrices, is not expected to perform equally well for cubic and noncubic crystal structures [41]. In addition, we note that DFT-DLM is a mean field theory, with the Weiss fields in Eq. (3) driving the magnetic ordering and vice versa. With these caveats in mind, we expect trends calculated across a series to be more robust than absolute values of specific quantities.

III. SOLVING THE KOHN-SHAM-DIRAC EQUATION WITHIN THE LSIC-LSDA

A. Relativistic DFT-DLM calculations

The large atomic number of the REs necessitates the use of relativistic (R) DFT-DLM theory to describe the spin-orbit coupling inherent in RE-TM magnets as well as mass-velocity and Darwin effects. Practically, our RDFT-DLM calculations involve two steps. In the first step, a self-consistent, scalar-relativistic DFT calculation is performed for a reference magnetic state. This reference magnetic state may be fully ordered (e.g., a ferromagnetic arrangement of spins) or fully disordered (the DLM/paramagnetic state). The output of this calculation is a set of atom-centered potentials. In the second step, these potentials are fed into the fully relativistic Kohn-Sham-Dirac (KSD) equation, thus treating spin-orbit coupling nonperturbatively. Combining the solutions of the KSD equation with the full KKR-CPA machinery allows the Weiss fields and $T_C$ to be computed. Although not a methodological necessity [42],
the potentials here are kept “frozen” in the second step, i.e.,
the density derived from the Green’s function of the partially
ordered system is not used to update the potentials.

When constructing the potentials in the first step, in common
with all DFT calculations it is necessary to make an approx-
imation for the exchange-correlation energy. The local-spin-
density approximation (LSDA) [44,43] performs rather well in
describing the magnetism of itinerant electrons, but struggles
to describe the strongly localized 4f states which characterize
REs [44]. Furthermore, the orbital moments of transition
metals are generally smaller than observed experimentally
when calculated within the LSDA [45]. As a result, it is
imperative to go beyond the LSDA exchange correlation when
modeling RE-TM magnets.

B. Treating RE-4f electrons

Recent computational works performed at zero temperature
have employed charge-self-consistent dynamical mean field
theory (DMFT) [46], in particular using the Hubbard-I
approximation [47], to calculate the magnetic moments of
REs [48] and RE-TM intermetallics like SmCo5 [49–51]
and NdFe12 [51]. The simpler, “open-core” scheme [52]
constrains the total spin density of the RE-4f electrons
to be that predicted by Hund’s rules [33,50,52–54]. Such
calculations, which provide much important insight into
RE-TM systems, bear some resemblance to crystal-field
theory in the sense that the RE-4f electrons are partitioned
from the rest of the material, with the amount of hybridization
they can undergo sensitive to how the calculation is set up
[51,53]. Alternative approaches like LDA/GGA+U [55–57],
the orbital polarization correction (OPC) [58], and the
self-interaction correction (SIC) [59] modify the potential at
the RE site but treat all electrons equally, in principle allowing
the RE-4f states to hybridize freely [55]. An advantage of
these schemes when studying trends across the RE-TM series
is that, beyond initial choices about how the schemes are
implemented, the calculations require minimal user input.
Indeed, the parameters entering the OPC and LDA/GGA+U
can be calculated from first principles, e.g., the Racah
parameters calculated from wave functions in the OPC [45],
or the U and J energies calculated from linear response [60]
or constrained random-phase approximation calculations [61].

The SIC, which we employ here, aims to ensure that the exchange-correlation potential cancels the electrostatic
(Hartree) energy of a single electron interacting with itself,
which is not automatically realized in the LSDA [44]. While
the scheme becomes more complicated in extended systems,
the localized nature of the RE-4f electrons makes them
particularly suitable for the SIC [59]. Furthermore, the SIC
has already been formulated within the KKR-CPA theory as
the local self-interaction correction (LSIC) [17]. Indeed, the
LSIC has been previously used in DFT-DLM calculations to
study Gd [18–21,38]. However, in order to treat an arbitrary RE
it is necessary to generalize the formalism. Conveniently, this
same formalism allows the OPC to be also incorporated in the
RDFT-DLM framework, facilitating an improved description
of the Co orbital moments.

C. An LSIC-LSDA scheme based on Hund’s rules

The LSIC formalism [17] is based on applying the self-
interaction correction to individual spin and orbital angular
channels, each characterized by the pair of quantum numbers
\( \sigma L, \sigma \) labels spin, and \( L \) is a composite quantum number
which, in principle, labels a member of any complete set of
angular momentum states. In the original LSIC implementa-
tion, these angular momentum states have the same symmetry
as the nonmagnetic crystal [17]. However, since the orbital
moments are largely unquenched in the RE-TM compounds,
here we choose \( L \) to label the “atomic” \((l,m)\) quantum
numbers associated with the complex spherical harmonics, i.e.,
eigenfunctions of the orbital angular momentum operator \( \hat{L}_z \).
As such, states that are degenerate in the nonmagnetic crystal
may be split by the LSIC.

We must also choose which spin and orbital angular
momentum channels we should apply the LSIC to. We propose
to follow the scheme illustrated in Fig. 2, which is inspired by
Hund’s rules. An extra LSIC channel is added for each RE-4f
electron, filling up \( \sigma L, \sigma \) labels spin, and \( L \) is a composite quantum number
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D. Including the LSIC/OPC in the KSD equation

The LSIC scalar-relativistic calculation (the first step re-
ferred to in Sec. III A) proceeds as described in Ref. [17]. At
the second step in the RDFT-DLM procedure (and at variance
with previous work [18–21,38]) the atom-centered potentials
have a contribution which depends on angular momentum,
conveniently written as

\[
V_{\text{SIC}}(r) = \sum_{L,\sigma} V^\sigma_{L}(r) \hat{P}_{L\sigma}.
\]
Here, $V_{L}^{\gamma}(r)$ is the spherically symmetric correction to the potential obtained in the scalar-relativistic calculation [17], while $\hat{P}_{L0}$ is a projection operator. In the Pauli representation these operators are $2 \times 2$ matrices which are diagonal for spin polarization along the $z$ axis, whose elements project out states with angular momentum character $L$.

The angular-momentum-dependent potentials result in a modified KSD equation

$$[\vec{a} \cdot \vec{p}c + \tilde{V}_{\text{SIC}} + \tilde{I}[V(r) - W] + \tilde{\beta}(\text{Im}c^2 + \tilde{\sigma}zB_{\text{XC}}(r))]\Psi = 0.$$  \tag{10}

Quantities with tildes are $4 \times 4$ matrices; $\Psi$ is a bispinor, and $W$ and $m$ the electron energy and rest mass. Compared to the usual KSD equation [62], Eq. (10) has an extra term $\tilde{V}_{\text{SIC}}$, simply related to $V_{\text{SIC}}$ in Eq. (9):

$$\tilde{V}_{\text{SIC}} = \begin{pmatrix} V_{\text{SIC}} & 0 \\ 0 & V_{\text{SIC}} \end{pmatrix}.  \tag{11}$$

We now follow the standard method of solving the radial KSD equation in multiple-scattering theory [63], i.e., we investigate the solutions

$$\Psi_{\nu}^{m_j}(r) = \sum_{\kappa_1} \left( \begin{array}{l} g_{\nu}^{m_j}(r) |x_{\kappa_1}^{m_j} \rangle \\ f_{\nu}^{m_j}(r) |x_{-\kappa_1}^{m_j} \rangle \end{array} \right).  \tag{12}$$

The spin-angular functions $|x_{\kappa_1}^{m_j} \rangle$ are superpositions of the products of Pauli spinors and spherical harmonics weighted by Clebsch-Gordan coefficients [62]. They are characterized by the quantum numbers $\kappa_1$ and $m_j$, and describe the angular character of free-particle solutions of the KSD equation, $\kappa_1$ is related to $j$, the sum of spin and orbital angular momentum in the spin-angular functions, with $\kappa = -l - 1$ for $j = l + 1/2$ and $\kappa' = l$ for $j = l - 1/2$. As indicated, we reserve the label $\kappa$ for negative values and $\kappa'$ for positive values of $\kappa_1$. The label $\nu$ denotes the different solutions required to build the Green’s function in scattering theory, i.e., solutions with an asymptotic free-electron character which are regular or irregular at the origin [63].

After inserting the trial solution (12) into Eq. (10) and performing a series of manipulations [62], we obtain coupled equations for the radial functions $f$ and $g$:

$$\frac{df_{\nu}^{m_j}(r)}{dr} = \frac{(\kappa - 1)}{r} f_{\nu}^{m_j} + \frac{1}{\hbar c}(V - E)g_{\nu}^{m_j}$$

$$+ \frac{1}{\hbar c} G_{\nu}^{m_j}((\kappa,\kappa')g_{\nu}^{m_j} + \frac{1}{\hbar c} G_{\kappa_1}(\kappa,\kappa')g_{\kappa_1}^{m_j}),$$

$$\frac{dg_{\nu}^{m_j}(r)}{dr} = \frac{-(\kappa + 1)}{r} g_{\nu}^{m_j} + \frac{1}{\hbar c} (E - V + 2mc^2)f_{\nu}^{m_j}$$

$$+ \frac{1}{\hbar c} G_{\nu}^{m_j}(-\kappa,-\kappa')f_{\nu}^{m_j}.  \tag{13}$$

Here, $E = W - mc^2$. The differential equations for $f_{\nu}^{m_j}$ and $g_{\nu}^{m_j}$ are obtained from Eqs. (13) simply by interchanging $\kappa$ and $\kappa'$. Crucially, compared to previous calculations which only included $B_{\text{XC}}$, the basic structure of the coupled equations (13) is unchanged by the addition of $V_{\text{SIC}}$. The difference is in the coupling functions

$$G_{\nu}^{m_j}(\kappa_1,\kappa_2) = \left\langle x_{\kappa_1}^{m_j} | (\sigma_{B_{\text{XC}}} \pm V_{\text{SIC}}) x_{\kappa_2}^{m_j} \right\rangle.  \tag{14}$$

$B_{\text{XC}}(r)$ is now augmented by a linear combination of the LSIC potentials $V^{m_j}_{\nu}(r)$ weighted by Clebsch-Gordan coefficients. We give the explicit form of these coupling functions in Appendix A, but here just show an example of $G_{\nu}^{m_j}(\kappa,\kappa)$ with $\kappa = -4$, $m_j = \frac{1}{2}$:

$$G_{\nu}^{1/2}(-4,-4) = \frac{1}{4} B_{\text{XC}} \pm \left\langle \frac{3}{4} V_{(3,0)}^{1/2} + \frac{1}{4} V_{(3,1)}^{1/2} \right\rangle.  \tag{15}$$

We see that the coupling functions can mix occupied, SI-corrected channels with unoccupied, non-SI-corrected channels, as discussed more in Appendix B.

The coupled equations (13), containing the appropriately weighted LSIC potentials, are solved numerically to give the scattering matrices and regular and irregular contributions to the Green’s function. From these quantities, the entire RDFT-DLM computational machinery [39] can be applied without further modification.

The OPC enters the KSD equation in exactly the same way as the LSIC. This is most easily seen by writing the OPC analogy of Eq. (9) as [54, 64]

$$V_{\text{OPC}}(\hat{r}) = \sum_{l=\pm \frac{1}{2}} \sum_{m,\sigma} -B_{l\sigma} m(\hat{P}_{l\sigma}) \hat{P}_{l\sigma},  \tag{16}$$

where $B_{l\sigma}$ is a Racah parameter, and $(\hat{P}_{l\sigma})$ is the spin-resolved expectation value for the relevant atom (we have anticipated applying the OPC to the d channel). Thus, the OPC can be considered a special case of the LSIC where the potential is independent of $r$, entering $G_{\nu}^{m_j}(\kappa_1,\kappa_2)$ weighted by the coefficients in Appendix A. We stress that, since they only modify the coupling functions, the computational cost of including the LSIC or OPC is negligible.

**E. Technical details**

We generated the atomic-centered potentials in the fully ordered (zero-temperature) state in self-consistent scalar-relativistic LSIC-LSDA calculations [17, 43] within the ASA, as implemented in the HUTSEPPot code [65]. Angular momentum expansions were truncated at $l_{\text{max}} = 3$, and the full Brillouin zone sampled on a $20 \times 20 \times 20$ grid with state occupancies determined by a Fermi-Dirac distribution with an electronic temperature of 400 K. The calculations were performed using experimental lattice constants [10, 13], which are listed in Table I together with the ASA radii for the three nonequivalent sites in the RECo$_5$ structure. We used the same relations between ASA radii as in our previous work on YCo$_5$ and GdCo$_5$ [19].

For the RDFT-DLM calculations, apart from the inclusion of the LSIC described above, we used the same computational setup (angular mesh, energy contour, electronic temperature) as in [19], including an adaptive sampling of the Brillouin zone [40]. We applied the LSIC to the RE-4f electrons and...
the OPC to the Co-3d electrons. The magnitude of the OPC was determined iteratively at 0 K with the magnetization aligned along the c axis, updating $\langle f^+_s \rangle$ at each iteration to self-consistency. The Racah parameters were calculated scalar relativistically. The same OPC was used for all temperatures, consistent with the frozen-potential approach.

IV. ZERO-TEMPERATURE CALCULATIONS

A. RECo$_5$ moments

We first use the RDFT-DLM formalism to calculate the magnetic moments of the RECo$_5$ series at zero temperature. To illustrate the trend across the lanthanide block, we consider all members of the RE = Y-Lu series, including the nonforming RE = Pm, Eu, Yb, and Lu compounds. Here, we fix the lattice parameters to those of GdCo$_5$; using the appropriate experimental RECo$_5$ lattice parameters (where available) produces very similar zero-temperature moments (Appendix C). For Ce, Pr, and Nd we also performed calculations without applying the LSIC (i.e., treating the $f$ electrons as itinerant).

In Fig. 3 we show the calculated RECo$_5$ moments and compare them to low-temperature experiments [10,13]. Here, the Co moments are aligned along the c axis, which defines the positive direction. A negative moment in Fig. 3 therefore means that the RE contribution to the magnetization is larger than that from the Co moments and is pointing in the opposite direction (RE dominated). Usually, experimental measurements (e.g., on powdered samples) only measure the absolute magnetization.

The variation in RECo$_5$ moment calculated with the LSIC (squares in Fig. 3) has a dramatic effect on the magnetization, for instance increasing the moment of CeCo$_5$ by 2$\mu_B$/formula unit (FU). Now, a strong variation with RE is observed, with PrCo$_5$/DyCo$_5$ achieving the largest TM/RE-dominated moments, respectively. The transition from TM- to RE-dominated magnetization occurs between Gd and Tb, and back to TM dominated between Er and Tm.

In order to decide whether the calculations with or without the LSIC should be used to describe a given RE, we examine the total energies calculated at the scalar-relativistic level omitting spin-orbit coupling effects. This approach follows, e.g., Refs. [17,67], where the comparison of SIC total energies was used to determine the volume triggering the $\alpha \rightarrow \gamma$ transition in Ce or the valency of the rare earths and their sulphides. We find that applying the LSIC to PrCo$_5$ and NdCo$_5$ lowers the total energy, i.e., it is energetically favorable. Indeed, for heavier REs the non-LSIC calculations become difficult to converge. However, applying the LSIC to CeCo$_5$ increases the scalar-relativistic total energy, indicating that the single Ce-4$f$ electron would prefer to be delocalized in this compound. Using this total energy as our criterion, we do not apply the LSIC to CeCo$_5$. Indeed, the picture of the itinerant Ce-4$f$ electron has already been established in previous theoretical work [68]. Other nonenergetically favorable calculations are shown in Fig. 3 as faint symbols.

The variation in RECo$_5$ moment calculated with the LSIC largely follows the simple picture presented in Fig. 2. In general, the antiferromagnetic RE-TM exchange interaction causes the RE spin moments to point in the opposite direction to the Co moments [69], but whether or not the total RE moment aligns parallel or antiparallel depends on the sign and magnitude of the orbital contribution [70]. The lightest REs have large orbital components pointing opposite to their spin which leads to parallel alignment of the total moments, whereas the spin and orbital moments of the heavy REs always reinforce each other to give antiparallel alignment.

![FIG. 3. Magnetic moments calculated at zero temperature with (squares) and without (crosses) the LSIC applied, compared to experimental values reported in Refs. [10] (circles) and [13] (stars). Faint symbols were calculated to be energetically unfavorable. The gray horizontal line at 8.78$\mu_B$ corresponds to the calculated YCo$_5$ moment.](224415-6)
TABLE II. Decomposition of zero-temperature moments. All quantities are in $\mu_B$. For comparison, we include the calculations for CeCo$_5$ with the LSIC applied (*) even though it is energetically unfavorable.

| RECo$_5$ | RE moment (spin/orbital/total) | Scalar rel. spin ($f/spd$) | Co moment (spin/orbital/total) | Total moment/FU | Exp. [10] | Exp. [13] |
|----------|-------------------------------|---------------------------|-------------------------------|----------------|----------|----------|
| YCo$_5$  | $-0.31/0.04/-0.28$            | $-0.31 (0.00/-0.31)$       | $7.54/1.25/8.78$              | 8.50           | 7.52     | 8.3      |
| LaCo$_5$ | $-0.30/0.04/-0.26$            | $-0.30 (-0.04/-0.25)$      | $7.11/1.19/8.30$              | 8.04           | 7.3      |          |
| CeCo$_5$ | $-0.92/0.51/-0.41$            | $-0.86 (-0.57/-0.29)$      | $7.07/1.40/8.47$              | 8.06           | 6.5      | 6.5      |
| CeCo$_5*$| $-1.37/2.97/1.60$             | $-1.37 (-1.07/-0.30)$      | $7.19/1.14/8.33$              | 9.93           | 6.5      | 6.5      |
| PrCo$_5$ | $-2.46/4.88/2.42$             | $-2.47 (-2.13/-0.34)$      | $7.25/1.06/8.31$              | 10.73          | 9.95     | 10.5     |
| NdCo$_5$ | $-3.56/5.74/2.18$             | $-3.58 (-3.32/-0.37)$      | $7.33/1.02/8.35$              | 10.53          | 10.6     | 10.5     |
| PmCo$_5$ | $-4.63/5.60/0.97$             | $-4.71 (-4.32/-0.39)$      | $7.38/0.97/8.35$              | 9.32           |          |          |
| SmCo$_5$ | $-5.63/4.55/-1.08$            | $-5.82 (-5.41/-0.40)$      | $7.36/0.85/8.21$              | 7.13           | 7.3      | 8.7      |
| EuCo$_5$ | $-6.60/2.60/-4.01$            | $-6.90 (-6.48/-0.42)$      | $7.36/0.95/8.32$              | 4.31           |          |          |
| GdCo$_5$ | $-7.50/0.03/-7.47$            | $-7.49 (-7.00/-0.49)$      | $7.43/1.27/8.70$              | 1.23           | 1.37     | 1.6      |
| TbCo$_5$ | $-6.42/-2.96/-9.38$           | $-6.41 (-5.98/-0.44)$      | $7.44/1.28/8.72$              | $-0.67$        | $-0.68$ | $-0.6$   |
| DyCo$_5$ | $-5.33/-4.93/-10.26$          | $-5.32 (-4.93/-0.39)$      | $7.46/1.28/8.75$              | $-1.52$        | $-1.1$  | $-1.2$   |
| HoCo$_5$ | $-4.26/-5.88/-10.14$          | $-4.20 (-3.86/-0.34)$      | $7.51/1.29/8.80$              | $-1.34$        | $-1.49$ | $-0.9$   |
| ErCo$_5$ | $-3.28/-5.89/-9.17$           | $-3.09 (-2.78/-0.31)$      | $7.40/1.27/8.67$              | $-0.50$        | 1.28     |          |
| TmCo$_5$ | $-2.27/-4.92/-7.19$           | $-2.00 (-1.71/-0.29)$      | $7.32/1.25/8.57$              | 1.38           | 2.2      |          |
| YbCo$_5$ | $-1.26/-2.95/-4.22$           | $-0.92 (-0.65/-0.27)$      | $7.30/1.24/8.53$              | 4.32           |          |          |
| LuCo$_5$ | $-0.29/0.04/-0.25$            | $-0.30 (-0.03/-0.27$       | $7.59/1.29/8.88$              | 8.63           |          |          |

B. Decomposition of RECo$_5$ moments

In Table II we resolve the calculated moments into spin and orbital contributions from the RE and TM. We also give the spin moments calculated at the scalar-relativistic level, which are further resolved into contributions of different angular momentum ($f$ or $spd$) character.

Concentrating first on the RE contribution to the magnetization, we see that the spin moments roughly track the expected spin of the LSIC channels, peaking at Gd. The scalar-relativistic decomposition shows the spin moments have an $spd$ component which increases from 0.25$\mu_B$ for La to 0.49$\mu_B$ for Gd. However, the $f$ components of the spin moment are not simply integers. Based on the simple picture of Fig. 2, this observation is surprising since we would expect each localized RE-4$f$ electron to contribute $\pm 1\mu_B$ to the magnetization. Instead, we see that for each additional LSIC channel the change in $f$ components is closer to $\pm 1\mu_B$, until the elements with filled spin subshells (GdCo$_5$ and LuCo$_5$) are reached. This behavior indicates that the nominally unoccupied RE-4$f$ states, which do not have the LSIC applied, are affecting the calculated properties.

The RE orbital moments also follow the general trend of Fig. 2, but are better described by $\mu_s = (2 - g_J)J$, where $g_J$ is the Landé factor [71]. This textbook expression is obtained by projecting the orbital moment onto the total angular momentum direction, which is valid for strong spin-orbit coupling. It is therefore natural to ask whether the spin RE moments should in fact be described by $\mu_s = 2(g_J - 1)J$, which is the corresponding projection for spin [71]. However, in our calculations the principal interaction affecting the spin moments is the scalar-relativistic exchange, which can be confirmed by noting the close agreement between the RDFT-DLM and scalar-relativistic spin moments in Table II. Therefore, the spin-orbit interaction plays a relatively minor role in determining the spin moment and the considerations leading to $\mu_s$ do not apply. We note that this situation is qualitatively different to the open-core scheme [52], which fixes the RE spin moments to $\mu_s$.

Now, considering the TM contribution to the magnetization, the most striking feature in Table II is the different behavior of the light and heavy RECo$_5$ compounds. The Co moments exhibit relatively small variations for the heavy REs except for LuCo$_5$ which, as already noted, behaves similarly to YCo$_5$. However, the variations for the light REs are much larger. Moving from La to Eu, the Co spin and orbital moments increase and decrease, respectively, and in general the total Co moments are smaller than for the heavy RECo$_5$ compounds. As we discuss in Sec. V, a qualitative difference in light and heavy RECo$_5$ behavior is also observed in $T_C$.

C. Comparison to experiment

When comparing to experiment, it is important to note that there is a sizable scatter in the published data. We have taken experimental low-temperature moments from the review articles of Refs. [10,13] which agree reasonably well with each other except for YCo$_5$ and SmCo$_5$, which deviate by approximately $1\mu_B$. Also, we note that the RE = Tb-Tm compounds do not form with exact RECo$_5$ stoichiometry. Instead, due to defects where the RE is substituted with pairs (dumbbells) of Co atoms [72], the compounds become increasingly Co rich. For example, the actual stoichiometry of the RE = Tm compound reported in Ref. [10] is TmCo$_4$.

With these limitations in mind, the calculations compare reasonably well to experiment in Fig. 3. Certainly, a number of qualitative features are reproduced, e.g., a drop in moment from Y to La, a large increase from Ce to Pr, and RE-dominated magnetization for Tb-Ho.

For the special case of CeCo$_5$, we note that the energetically unstable LSIC calculation gives a moment which is in qualitative disagreement with the experimental trend. Interestingly, however, while the LSDA+OPE calculations are closer to...
FIG. 4. Magnetization per formula unit calculated at different temperatures for the (a) light and (b) heavy RECo₅ compounds. Calculations were performed at the GdCo₅ lattice parameters.

experiment, they still overestimate the CeCo₅ moment. Not including the OPC on the Co atoms rather improves the agreement (Ref. [68] and Appendix C), suggesting that (like for the LSIC) there might be a criterion based on energetics to decide whether or not the OPC should be applied.

Apart from the cases of ErCo₅ and TmCo₅ where the experiments are Co rich, the remaining compound where the discrepancy between calculations and experiment is quite large is SmCo₅, specifically compared to the value of 8.7μ_B/FU in Ref. [13]. Interestingly, a recent neutron diffraction experiment reported even larger local moments in SmCo₅, which add up to give a resultant magnetization in excess of 12μ_B/FU [73].

Studies employing DMFT and open-core calculations have reported smaller Sm total moments of approximately −0.3μ_B, which would bring the total SmCo₅ moment closer to 8μ_B/FU [49–51]. Earlier GGA+U calculations found a much larger total moment of 9.9μ_B/FU due to a ferromagnetic alignment of Sm and Co spins. The scatter in theoretical and experimental data hints at the richness of the physics of SmCo₅ which, as we show next, is also seen in $T_C$.

V. FINITE-TEMPERATURE CALCULATIONS

A. Magnetization vs temperature curves

We now include local moment disorder within the RDFT-DLM picture. Figures 4(a) and 4(b) show the magnetization versus temperature ($M_vT$) curves calculated for light and heavy RECo₅ compounds. These calculations were performed at the GdCo₅ lattice constants (Table I). The light REs show behavior associated with ferromagnets, i.e., a monotonic decrease in magnetization with increasing temperature. By contrast, the heavy RECo₅ compounds have magnetizations which initially become more positive (TM dominated) as the temperature increases, before reducing at higher temperatures. As we have shown previously by comparing YCo₅ and GdCo₅ [19], this contrasting behavior is due to the RE moments disordering more quickly with temperature compared to the antiferromagnetically aligned Co sublattice. As a result, the strong negative contribution to the total magnetization from the heavy RE diminishes quickly, leaving the positive Co magnetization.

In the case that the zero-temperature magnetization is RE dominated, there is a compensation temperature at which the strongly disordered RE magnetization cancels the weakly disordered Co magnetization. Our calculated compensation temperatures are 84 K (TbCo₅), 85 K (DyCo₅), 45 K (HoCo₅), and 19 K (ErCo₅). Reference [10] reports experimental compensation temperatures of 110 K (TbCo₅), 123 K (DyCo₅), and 71 K (HoCo₅).

We note that the calculated $M_vT$ curves have finite slopes at $T = 0$ K, while experimentally measured curves tend to be flat [19]. The origin of this discrepancy is the classical statistical mechanics used in the DLM picture [Eq. (3)], which does not give an energy barrier between the zero-temperature arrangement of local moments and an excited state where the moments have undergone infinitesimal rotations.

B. RE order parameters

In order to analyze the RE contribution to the magnetization in more detail, in Figs. 5(a) and 5(b) we plot the temperature evolution of the RE order parameter $m_{RE}$ [Eq. (8)]. The heaviest REs Ho, Er, and Tm disorder very quickly with temperature, losing 50% of their ordering below 200 K. By contrast, the Sm sublattice retains its ordering to much higher temperatures, e.g., 50% ordering at 650 K. Although part of the reason for this behavior is the higher $T_C$ of SmCo₅, plots of the order parameter against reduced temperature $T/T_C$ (not shown) demonstrate that even when this factor is accounted for, Sm orders the most strongly.

Having an ordered RE at high temperature is useful for permanent magnets since the magnetocrystalline anisotropy decays faster than $m_{RE}$ [9]. Therefore, SmCo₅ has a double advantage of having a high magnetocrystalline anisotropy at low temperature, and a strong RE ordering to retain this anisotropy at high temperature.

C. Curie temperatures

In Fig. 6(a) we compare the calculated Curie temperatures $T_C$ (extracted from Fig. 4) to the experimental values reported in Ref. [10]. We include $T_C$ calculated for the nonforming Pm, Eu, Yb, and LuCo₅ compounds. We remind the reader that experimental values are for Co-rich heavy RECo₅ compounds, for which we would expect an increased $T_C$. For instance, the measured $T_C$ of Gd₂Co₁₇ is 200 K higher than GdCo₅ [10].
Figure 6(a) clearly shows the contrasting behavior of the light and heavy RECo$_5$ compounds. Apart from YCo$_5$ and CeCo$_5$, the $T_C$ of the light RECo$_5$ compounds increases monotonically with the number of RE-4$f$ electrons. Indeed, applying the energetically unfavorable LSIC to the Ce-4$f$ electron also causes CeCo$_5$ to follow this trend [faint square in Fig. 6(a)]. Of the experimentally known RECo$_5$ compounds, SmCo$_5$ is calculated to have the highest $T_C$ (942 K), but the $T_C$ of the nonforming EuCo$_5$ compound is found to be even higher, at 973 K.

The trend in calculated $T_C$ of the heavy RECo$_5$ compounds is less obvious. In general, filling the remaining subshell causes a reduction in $T_C$, but a secondary peak is observed at HoCo$_5$. This peak in $T_C$ coincides with a slight peak in Co moments for HoCo$_5$ at zero temperature (Table II). Also, the $T_C$ of the nonforming EuCo$_5$ compound is found to be even higher, at 973 K.

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The calculated variation in $T_C$ shown in Fig. 6(a) is only due to changing the RE. In order to quantify the magnetostructural effect of varying the lattice, we also calculated $T_C$ for the RECo$_5$ compounds using experimentally reported lattice parameters (Table I). We further performed calculations where we varied the lattice but fixed the RE to Gd, i.e., GdCo$_5$ on different RECo$_5$ lattices. We compare the three different sets of calculations in Fig. 6(b).

First considering the calculations with the RE fixed to Gd [red circles in Fig. 6(b)], we observe a decrease in $T_C$ across the lanthanide block. The exception is CeCo$_5$, which shows a strong magnetostructural effect; as shown in Table I, CeCo$_5$ has an anomalously small a parameter. These calculations do not reproduce experimental trends, e.g., predicting LaCo$_5$ to have the highest $T_C$.

If instead we vary both the RE and the lattice parameters [blue crosses in Fig. 6(b)] we find an almost identical trend in $T_C$ as if we had kept the lattice parameters fixed at GdCo$_5$ (green squares). Using the RECo$_5$ lattice parameters accentuates the drop in $T_C$ for CeCo$_5$. Unfortunately, the experimentally observed difference in $T_C$ between YCo$_5$ and LaCo$_5$ is no longer calculated, which can be seen as a cancellation of competing green and red symbols in Fig. 6(b). In general, the calculations find magnetostructural effects to play
a less important role in determining $T_C$ than explicitly varying the RE.

D. Order-parameter expansion of the free energy

Returning to the calculations with the lattice constants fixed to GdCo$_5$, to gain further insight into the calculated $T_C$ we expand the RDFT-DLM potential energy $\langle \Omega \rangle_{0,T}$ in terms of the order parameters $m_{\text{RE}}, m_{\text{CoI}},$ and $m_{\text{CoII}}$ [19]. The labels I and II distinguish between the inequivalent Co positions in the RECo$_5$ structure (Fig. 1), i.e., the two Co atoms in plane with the RE (Co$_I$, Wyckoff position 2c) and the three out-of-plane Co atoms (Co$_{III}$, Wyckoff position 3g). In this expansion, the Weiss field at each site $(h_{\text{RE}}, h_{\text{CoI}}, h_{\text{CoII}})$ is given by the equation

$$
\frac{1}{2} (h_{\text{RE}}) = \left( \begin{array}{ccc}
J_{\text{RE-RE}} & J_{\text{RE-CoI}} & J_{\text{RE-CoII}} \\
J_{\text{RE-CoI}} & J_{\text{CoI-CoI}} & J_{\text{CoI-CoII}} \\
J_{\text{RE-CoII}} & J_{\text{CoI-CoII}} & J_{\text{CoII-CoII}}
\end{array} \right) \left( \begin{array}{c}
m_{\text{RE}} \\
m_{\text{CoI}} \\
m_{\text{CoII}}
\end{array} \right).$

The prefactors in the Weiss fields account for the site multiplicities. The expansion of Eq. (17) is valid for small $m$, i.e., close to $T_C$. The coefficients $J_{XY}$ are obtained by least-squares fitting of RDFT-DLM calculations. As discussed in Ref. [19], diagonalization of the matrix in Eq. (17) gives the RDFT-DLM $T_C$, thus allowing the variation shown in Fig. 6(a) to be understood in terms of the strength of the interactions between different magnetic sublattices.

The calculated coefficients $J_{XY}$ are shown in Fig. 7. A negative $J_{XY}$ indicates a tendency for the spins of species $X$ and $Y$ to align antiferromagnetically. Comparing Figs. 6(a) and 7, we see that the behavior of $T_C$ is mirrored by the largest $J_{XY}$ coefficient $J_{\text{CoI-CoII}}$, which describes the interlayer Co interaction. The next-largest coefficient $J_{\text{CoI-CoI}}$, describing the intralayer interactions of the pure Co layer, behaves similarly except that no drop at CeCo$_5$ is observed. It is not surprising either that $T_C$ tracks the largest $J_{XY}$ coefficients or that these coefficients describe Co-Co interactions, in line with the picture that the TM is responsible for the high $T_C$ in RE-TM magnets. What is less intuitive is that these coefficients should be so strongly affected by the RE.

As found for $T_C$, there is clear distinction between light and heavy RECo$_5$ compounds for $J_{\text{CoI-CoI}}$ and $J_{\text{CoI-CoII}}$. By contrast, $J_{\text{CoII-CoII}}$ undergoes a general decrease from La-Lu, with slight fluctuations around Ho and a dip at Ce. The Co interactions are very similar for Y and Lu, consistent with their similar $T_C$.

The $J_{\text{RE-TM}}$ coefficients which quantify RE interactions are smaller in magnitude. $J_{\text{RE-Co}}$ is particularly weak and correlates with the size of the spin moment of the RE. The strongest RE-Co interactions are interplanar, RE-Co$_{III}$. Interestingly, neither $J_{\text{CoI-CoI}}$ nor $J_{\text{RE-CoI}}$ show any strong anomaly at CeCo$_5$, indicating that it is only the Co$_I$ interactions which are affected by the itinerant Ce-4$f$ electron.

Again comparing the light and heavy REs, we note that the in-plane interaction quantified by $J_{\text{RE-CoI}}$ actually becomes ferromagnetic for DyCo$_5$, HoCo$_5$, and ErCo$_5$, which coincides with the secondary peak in $T_C$ [Fig. 6(a)]. Also, we observe that the strongest RE-Co interactions occur not for GdCo$_5$, which has the largest RE spin moment, but rather EuCo$_5$.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{Different $J_{XY}$ parameters [cf. Eq. (17)] calculated for RECo$_5$ on the GdCo$_5$ lattice. Note that the Ce calculation was performed without the LSIC, i.e., assuming that the Ce $f$ electron is itinerant. We highlight $J_{XY}$ for YCo$_5$ as crosses with horizontal dashed lines.}
\end{figure}

VI. DISCUSSION

A. RE-TM interaction

Our calculations have found that the strength of magnetic interactions between Co moments in RECo$_5$ is affected by the RE, even when the lattice parameters are held fixed. As a result of this variation, $T_C$ depends heavily on the RE. To explain this behavior, we first recall the theory of RE-TM interactions described in Ref. [69], which explains the antiferromagnetic spin coupling in terms of hybridization between RE-5d and TM-3d states. Figure 8 is a schematic representation of the theory. The magnetic properties of Co originate from almost-full and almost-empty 3d bands of opposing spins. The minority spin Co-3d band lies closer in energy to the RE-5d bands than the majority Co-d band, and therefore hybridizes more strongly. The preferential occupation of the lower-energy
hybridized spin states causes the RE-5d bands to develop a
spin polarization in the direction of the Co minority spin,
\( \text{i.e., an antiferromagnetic coupling. Then, onsite RE} \) 4f-5d
interactions polarize the RE-4f spins in the same sense.

In this picture, the RE-TM interaction varies according to
the strength of the 4f-5d interaction, which is expected to scale
with the spin moment of the RE. Accordingly, the strongest RE-
TM interactions are expected for Gd. However, any effects on
the TM magnetization are expected to proceed via the Co-3d–
RE-5d hybridization, with no direct link to the RE-4f states.

### C. Densities of states

In Fig. 9(a) we plot the DFT Kohn-Sham density of states (DOS) of SmCo5. The DOS was calculated just below \( T_C \)
(i.e., at an almost completely disordered state), using GdCo5
lattice parameters, and has been resolved into contributions
from the RE, CoI, and CoII sublattices. The wide energy scale
of Fig. 9(a) was chosen to show explicitly the energy position of
the occupied Sm-4f states, 11 eV below the Fermi level \( E_F \).
Zooming in on the region around \( E_F \) [Fig. 9(b)] shows the
Co-3d band (bandwidth \( \sim 4 \) eV) hybridized with the RE-5d
states. However, an additional prominent feature is observed
in the RE DOS, which is a narrow peak above \( E_F \). The weight
of this peak is approximately two electrons, and corresponds
to the two unoccupied RE-4f states in the \( \downarrow \) spin channel (Fig. 2).

A similar peak can be observed in the DOS of all the RECo5
compounds. For REs with almost empty 4f spin subshells,
the peak is located at high energy, and comes closer to \( E_F \)
as the subshell becomes filled.\(^1\) We stress that in our DFT
description, states above \( E_F \) make no contribution to calculated
properties. However, the tail of this unoccupied RE-4f peak
does extend below \( E_F \) and therefore contributes to the density.
In fact, this tail is the origin of the noninteger contribution to
the \( f \)-resolved spin moments pointed out in Sec. IV B when
discussing Table II.

As indicated in Fig. 9(b), we can extract the energy corres-
ponding to the center of this unoccupied peak (dashed line).
Then, in Fig. 9(c) we plot the calculated \( T_C \) as a function of
this peak position. The light REs show an apparently
strong correlation, with \( T_C \) increasing as the unoccupied peak
becomes closer to \( E_F \). By contrast, the heavy REs do not show
any particular correlation. The possible exception is HoCo5,
which as well as having a higher \( T_C \) than its neighbors also has
the unoccupied RE-4f peak closest to \( E_F \).

An explanation for the differing behavior of the light and
heavy RECo5 compounds in Fig. 9(c) relates to the spin
character of the unoccupied peak. For the light REs, the
unoccupied RE-4f peak closest to \( E_F \) has the same \( \downarrow \) spin
as the Co-3d minority spins, \( \text{i.e., the states which hybridize} \)
strongly with the RE-5d states and lead to antiferromagnetic
coupling (Fig. 8). By contrast, the unoccupied RE-4f peak
of the heavy REs has the same \( \uparrow \) spin character as the Co-d

\(^1\)For light REs, a second peak corresponding to the opposite spin
channel is also present, at much higher energies.
FIG. 9. DOS calculated just below $T_C$ for SmCo$_5$, resolved onto the Sm, CoI, and CoII sublattices, shown (a) across a wide energy scale and (b) around the Fermi energy. The vertical dashed line intersects the center of the unoccupied 4$f$ peak above the Fermi energy. (c) $T_C$ plotted against the center of this unoccupied peak for the different RECo$_5$ compounds. Note that here the value of $T_C$ of CeCo$_5$ was calculated with the LSIC applied.

We therefore propose a mechanism where a small contribution of 4$f$-character RE states, located just below the Fermi level, affects $T_C$ by modifying the Co-3$d$ states, probably indirectly through the RE-5$d$ states. Such a mechanism could explain why we calculate higher $T_C$'s than GdCo$_5$ for Pm, Sm, and EuCo$_5$, despite these elements having smaller spin

majority spins. The hybridization of these states with RE-5$d$ is weak due to the energy separation; also, it favors ferromagnetic coupling. As noted when discussing Fig. 7, HoCo$_5$ does indeed have a positive $J_{RE-CoI}$ coefficient, corresponding to a ferromagnetic RE-TM interaction. Indeed, the temperature evolution of the order parameters in Fig. 5 shows how the overall antiferromagnetic RE-TM coupling is weakened for the heavy RECo$_5$ compounds. We note that here the value of $T_C$ of CeCo$_5$ was calculated with the LSIC applied.

VII. OUTLOOK

We have devised a physically transparent theory to model the magnetic properties of RE-TM compounds, with particular emphasis on their finite-temperature properties. The magnetic disorder is described with the disordered local moment picture based on relativistic density functional theory, with the RE-4$f$ electrons treated with the local self-interaction correction which encapsulates Hund’s rules. We used the theory to calculate the zero- and finite-temperature properties of the RECo$_5$ family of magnets, comparing magnetic moments and Curie temperatures to experimental measurements.

When presenting our theory we stated that, mainly as a result of the spherical approximations and mean field nature of the theory, we expected our approach to perform best in calculating trends across a series. This statement has been borne out by our comparisons with experimental data, where we were able to reproduce a number of qualitative features. In particular, we were able to track the behavior of $T_C$, which to our knowledge has never been accomplished from first principles before.

We identified interesting behavior from the calculations, that even though $T_C$ is generally determined by TM-TM interactions, these interactions were nonetheless affected by the RE. We argued that while the varying spatial extent of the RE-5$d$ orbitals did affect the TM-TM interactions, this effect was not sufficient to explain the variation in $T_C$. Instead, we proposed a mechanism based on a small $f$-character contribution to the density around the Fermi level which, for the light RECo$_5$ compounds, strengthens both the RE-TM and TM-TM interactions.

We note that more expensive DMFT calculations do not provide an obvious pathway for a further exploration of this mechanism, neither in being able to calculate $T_C$, nor also since we cannot make any assumptions about the hybridization of the RE-4$f$ electrons [51]. In terms of experimental evidence, we currently have only the observation that SmCo$_5$ has a higher $T_C$ than GdCo$_5$. To our knowledge, this observation has not been explained before, but on its own cannot be considered justification for the correctness of the LSIC. However, the theory presented here opens the door to performing a more detailed comparison with experimental measurements on the moments and being placed on a lattice with a compressed $a$ parameter. The effect is strong (weak) for the light (heavy) RECo$_5$ compounds, and favors antiferromagnetic (ferromagnetic) RE-TM coupling as described above, consistent with the behavior of $J_{RE-CoI}$ and $J_{RE-CoII}$ shown in Fig. 7.

We have already pointed out that the calculations have found SmCo$_5$ both to have the highest $T_C$ of the experimentally realized RECo$_5$ compounds and also a strong RE-TM interaction, which enables Sm to stay ordered at high temperature. Within the mechanism described here, the origin of this behavior is Sm’s almost-filled 4$f$ spin subshell. The hypothetical EuCo$_5$ compound would have an even higher $T_C$, but unfortunately does not form. The total energies calculated at the scalar-relativistic level find Eu to be more stable in the 3$^+$ state, which when forced to occupy the RECo$_5$ structure. However, we have not investigated the full compositional phase diagram where different stoichiometries and structures might have a lower free energy.
temperature-dependent properties of any RE-TM compound, as was already done for YCo$_5$ and GdCo$_5$ [19].

Beyond exploring the fundamental physics of RE-TM magnets, our theoretical framework allows the study of practical aspects. In particular, the CPA formalism allows the effects of compositional disorder, e.g., substitution of RE or TM elements, to be investigated. Furthermore, with a view to optimizing high-temperature coercivity, it is highly desirable to tackle the temperature dependence of the magnetocrystalline anisotropy [37]. Such calculations require a careful incorporation of crystal-field effects into our ASA calculations [75] and also special care regarding how the calculated quantities are compared to experimental measurements, given the ferrimagnetic nature of the RE-TM magnets [38]. Already, the current calculations have found the high-temperature RE magnetic ordering to be strongest in SmCo$_5$, the best-performing magnet in the RECo$_5$ family.

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APPENDIX A: COUPLING INTRODUCED BY THE LSIC

Here, we list the formulas for the different coupling functions which enter the coupled equations (13). Again, we emphasize that $\kappa = -l - 1$ and $\kappa' = l$. We have also introduced the quantities $\tilde{l}_1 = l + 1$ and $\tilde{l}_2 = l - 1$:

$$
\mathcal{G}_{\pm}^{m,l}(\kappa,\kappa) = \frac{2m_j}{2l + 1} B_{XC} \pm \left[ V_{\tilde{l}_1(l,m_j-1/2)} \left( l + m_j + 1/2 \right) + 2l + 1 \right] + \left[ V_{\tilde{l}_1(l,m_j+1/2)} \left( l - m_j + 1/2 \right) + 2l + 1 \right],
$$

$$
\mathcal{G}_{\pm}^{m,l}(\kappa',\kappa') = -\frac{2m_j}{2l + 1} B_{XC} \pm \left[ V_{\tilde{l}_1(l,m_j-1/2)} \left( l - m_j + 1/2 \right) + 2l + 1 \right] + \left[ V_{\tilde{l}_1(l,m_j+1/2)} \left( l + m_j + 1/2 \right) + 2l + 1 \right],
$$

$$
\mathcal{G}_{\pm}^{m,l}(\kappa,\kappa') = -\left[ 1 - \frac{m_j^2}{l(l+1/2)^2} \right] \frac{B_{XC}}{2} \pm \frac{V_{\tilde{l}_1(l,m_j-1/2)} - V_{\tilde{l}_1(l,m_j+1/2)}}{2},
$$

$$
\mathcal{G}_{\pm}^{m,l}(-\kappa,-\kappa) = -\frac{2m_j}{2l + 1} B_{XC} \pm \left[ V_{\tilde{l}_1(l,m_j-1/2)} \left( \tilde{l}_1 - m_j + 1/2 \right) + 2l + 1 \right] + \left[ V_{\tilde{l}_1(l,m_j+1/2)} \left( \tilde{l}_1 + m_j + 1/2 \right) + 2l + 1 \right],
$$

$$
\mathcal{G}_{\pm}^{m,l}(-\kappa',-\kappa') = -\frac{2m_j}{2l + 1} B_{XC} \pm \left[ V_{\tilde{l}_1(l,m_j-1/2)} \left( \tilde{l}_2 - m_j + 1/2 \right) + 2l + 1 \right] + \left[ V_{\tilde{l}_1(l,m_j+1/2)} \left( \tilde{l}_2 + m_j + 1/2 \right) + 2l + 1 \right].
$$

FIG. 10. Spin-resolved, zero-temperature DOS for SmCo$_5$ (left) and DyCo$_5$ (right), at energies corresponding to the majority-spin, SI-corrected states. The majority- and minority-spin contributions are plotted with positive and negative signs, respectively, and the lower plots zoom in on the minority contribution. Note the larger scale for DyCo$_5$. 
APPENDIX B: RELATIVISTIC COUPLINGS BETWEEN DIFFERENT SPIN-ORBITAL CHANNELS

As indicated by Eq. (15), the spin-orbit interaction mixes different ($\sigma, m$) channels, including those which do and do not have the LSIC applied. In general, since there is a large energy separation between corrected and uncorrected states ($\sim 10$ eV), the energy denominator that appears in the perturbative expansion of the state is large and thus the mixing is small. Nonetheless, the mixing can be seen by examining the zero-temperature, spin-resolved DOS at energies around the occupied (majority spin) 4$f$ electrons.

This quantity is plotted in Fig. 10 for SmCo$_5$ and DyCo$_5$.

In the scalar-relativistic calculation, the occupied 4$f$ electrons are spin pure, but on performing the relativistic calculation a small contribution appears in the minority-spin channel (negative scale in Fig. 10), due to the mixing described above. This contribution is bigger for DyCo$_5$ than SmCo$_5$ (note change of scale) because there are two SI-corrected minority-spin states located 4 eV above the majority-spin peak which mix more strongly. For SmCo$_5$, the mixing only occurs with SI-uncorrected states lying above the Fermi level. The large energy separation suppresses the mixing in this case.

APPENDIX C: ZERO-TEMPERATURE MOMENTS CALCULATED AT EXPERIMENTAL LATTICE PARAMETERS

In Fig. 11, we compare the zero-temperature moments calculated either using GdCo$_5$ lattice parameters or, where available, RECo$_5$ lattice parameters (Table I). Note that these calculations were performed without the OPC applied, which results in reduced Co moments compared to Fig. 3.

[1] R. J. Elliott, in Magnetic Properties of Rare Earth Metals, edited by R. J. Elliott (Plenum, London, 1972), p. 1.
[2] D. C. Koskenmaki and K. A. Gschneidner, Jr., in Handbook of the Physics and Chemistry of Rare Earths, edited by K. A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1978), p. 337.
[3] V. Zepf, Rare earth elements: What and where they are, in Rare Earth Elements: A New Approach to the Nexus of Supply, Demand and Use: Exemplified along the Use of Neodymium in Permanent Magnets (Springer, Berlin, 2013), pp. 11–39.
[4] K. Strnat, G. Hoffer, J. Olson, W. Ostertag, and J. J. Becker, J. Appl. Phys. 38, 1001 (1967).
[5] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, and Y. Matsuura, J. Appl. Phys. 55, 2083 (1984).
[6] J. J. Croat, J. F. Herbst, R. W. Lee, and F. E. Pinkerton, J. Appl. Phys. 55, 2078 (1984).
[7] O. Guttfleisch, M. A. Willard, E. Brück, C. H. Chen, S. G. Sankar, and J. P. Liu, Adv. Mater. 23, 821 (2011).
[8] J. M. D. Coey, IEEE Trans. Magn. 47, 4671 (2011).
[9] M. D. Kuz'min and A. M. Tishin, in Handbook of Magnetic Materials, edited by K. H. J. Buschow (Elsevier, Amsterdam, 2008), Vol. 17, Chap. 3, p. 149.
[10] K. H. J. Buschow, Rep. Prog. Phys. 40, 1179 (1977).
[11] S. Chikazumi, Physics of Ferromagnetism, 2nd ed. (Oxford University Press, Oxford, 1997), p. 62.
[12] Z. Tie-song, J. Han-min, G. Guang-hua, H. Xiuc-feng, and C. Hong, Phys. Rev. B 43, 8593 (1991).
[13] A. V. Andreev, in Handbook of Magnetic Materials, edited by K. H. J. Buschow (North-Holland, New York, 1995), Vol. 8, Chap. 2, p. 59.
[14] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
[15] B. L. Györfy, A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, J. Phys. F: Met. Phys. 15, 1337 (1985).
[16] J. B. Staunton, L. Szyynyogh, A. Buruzs, B. L. Györfy, S. Ostanin, and L. Udvardi, Phys. Rev. B 74, 144411 (2006).
[17] M. Lüders, A. Ernst, M. Dänz, Z. Szotek, A. Svane, D. Ködderitzsch, W. Hergert, B. L. Györfy, and W. M. Temmerman, Phys. Rev. B 71, 205109 (2005).
[18] E. Mendive-Tapia and J. B. Staunton, Phys. Rev. Lett. 118, 197202 (2017).
[19] C. E. Patrick, S. Kumar, G. Balakrishnan, R. S. Edwards, M. R. Lees, E. Mendive-Tapia, L. Petit, and J. B. Staunton, Phys. Rev. Mater. 1, 024411 (2017).
[20] L. Petit, D. Faudyal, Y. Mudryk, K. A. Gschneidner, V. K. Pecharsky, M. Lüders, Z. Szotek, R. Banerjee, and J. B. Staunton, Phys. Rev. Lett. 115, 207201 (2015).
[21] I. D. Hughes, M. Dänz, A. Ernst, W. Hergert, M. Lüders, J. Poulter, J. B. Staunton, A. Svane, Z. Szotek, and W. M. Temmerman, Nature (London) 446, 650 (2007).
[22] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. 73, 515 (2001).
[23] F. Giustino, Rev. Mod. Phys. 89, 015003 (2017).
[24] J. B. Staunton, Rep. Prog. Phys. 57, 1289 (1994).
[25] A. J. Cohen, P. Mori-Sánchez, and W. Yang, Science 321, 792 (2008).
[26] F. Illas, I. de P. R. Moreira, J. M. Bofill, and M. Filatov, Phys. Rev. B 70, 132414 (2004).
[27] A. Liechtenstein, M. Katsnelson, V. Antropov, and V. Gubanov, J. Magn. Magn. Mater. 67, 65 (1987).
[28] K. Cao, G.-C. Guo, D. Vanderbilt, and L. He, Phys. Rev. Lett. 103, 257201 (2009).
