Intrinsically weak magnetic anisotropy of cerium in potential hard-magnetic intermetallics

Anna Galler,1 Semih Ener,2 Fernando Maccari,2 Imants Dirba,2 Konstantin P. Skokov,2 Oliver Gutfleisch,2 Silke Biermann,1,3,4,5 and Leonid V. Pourovskii1,3

1Centre de Physique Théorique, Ecole Polytechnique, CNRS, Institut Polytechnique de Paris, 91128 Palaiseau Cedex, France
2Functional Materials, Department of Material Science, Technische Universität Darmstadt, 64287, Darmstadt, Germany
3Collège de France, 11 place Marcelin Berthelot, 75005 Paris, France
4Department of Physics, Division of Mathematical Physics, Lund University, Professorsgatan 1, 22363 Lund, Sweden
5European Theoretical Spectroscopy Facility, 91128 Palaiseau, France, Europe

Cerium-based intermetallics are currently attracting much interest as a possible alternative to existing high-performance magnets containing scarce heavy rare-earth elements. However, the intrinsic magnetic properties of Ce in these systems are poorly understood due to the difficulty of a quantitative description of the Kondo effect, a many-body phenomenon where conduction electrons screen out the Ce-4f moment. Here, we show that the Ce-4f shell in Ce-Fe intermetallics is partially Kondo screened. The Kondo scale is dramatically enhanced by nitrogen interstitials completely suppressing the Ce-4f contribution to the magnetic anisotropy, in striking contrast to the effect of nitrogenation in isostructural intermetallics containing other rare-earth elements. We determine the full temperature dependence of the Ce-4f single-ion anisotropy and show that even unscreened Ce-4f moments contribute little to the room-temperature intrinsic magnetic hardness. Our study thus establishes fundamental constraints on the potential of cerium-based permanent magnet intermetallics.

I. INTRODUCTION

The last decades have witnessed a rapidly growing demand for energy-efficient technologies, from optimized power generation and conversion devices to new transportation solutions. A key component ingredient of motors, generators, sensors, or actuators are high-performance permanent magnets. Identifying and designing improved materials for permanent-magnet applications has thus the potential of huge economical and environmental savings.12 Today, the world market for permanent magnets in the more advanced applications is largely dominated by rare-earth based materials: the best hard-magnetic materials are based on the Nd-Fe-B ”2-14-1” system whose extraordinary hard-magnetic properties are further boosted by partially substituting Nd with heavy rare-earth elements like Dy or Tb. In such rare-earth-transition-metal intermetallics, the electronic structure of the transition metal sublattice provides a large magnetization and high Curie temperature. The intrinsic magnetic hardness \( \kappa \) is due to the rare-earth local magnetic moment, which—due to the large spin-orbit coupling acting on the rare-earth electronic states—effectively converts the crystalline anisotropy into single-ion magnetic anisotropy.13

Available resources of heavy rare-earths are scarce, thus motivating efforts to replace them with so-called rare earth balance magnets, containing more abundant rare-earth elements, in particular Ce.11,14,17 A significant limitation to the magnetic hardness of Ce-transition metal intermetallics is caused by the well-known tendency of Ce-4f electrons to form heavy-electron itinerant bands, as for instance observed in so-called ”heavy fermion” compounds.14 Indeed, in the heavy-fermion regime the Ce local magnetic moment is screened by conduction electrons, which couple to the single Ce-4f electron to form a nonmagnetic singlet state. Such a heavy-fermion behavior of Ce has been observed in the ”1-5” (RC05, \( R = \) rare-earth) and ”2-14-1” (\( R_2Fe_14B \)) families of hard-magnetic intermetallics19 compromising, in particular, the utility of \( Ce_2Fe_14B \) for magnetic applications.11

In order to possess a significant single-ion magnetic anisotropy, an obvious conditio sine qua non is that the 4f electron of Ce needs to be localized and its magnetic moment not significantly Kondo-screened. A reliable quantitative assessment of localized vs. heavy-fermion behavior of the Ce-4f electrons is thus key to a successful theoretical search for prospective hard-magnetic cerium intermetallics. Such an assessment represents a formidable theoretical challenge as the formation of a heavy-fermion state in Ce-based compounds is a genuine non-perturbative many-body phenomenon that requires a description beyond density functional theory (DFT) or DFT+U techniques.12,13 At present, these limitations seriously hamper the possibilities of computational materials design in the field (see e.g. Ref.14).

Here, we address this challenge by developing an ab initio approach to the magnetocrystalline anisotropy of Ce-based intermetallics. We describe the electronic structure of magnetic Ce transition metal intermetallics using advanced many-body electronic structure methods that take into account the effect of the Kondo screening. Furthermore, we supplement this first-principles framework
FIG. 1: Crystal structure, Ce magnetism and Kondo effect in Ce-Fe "1-12". (a) Tetragonal body-centered crystal structure of CeFe11TiN (space group I4/mmm). (b) Quasi-atomic approximation to the Ce magnetism. The Ce-4f spins are aligned anti-parallel with respect to the Fe moments due to the exchange field $B_{ex}$. The magnitude of the Ce magnetic moment in this quasi-atomic picture is determined by $B_{ex}$ and the crystal-field splitting on the Ce-4f shell. (c) Many-electron effects drastically alter this picture: the Kondo screening (green cloud) reduces the Ce magnetic moment concomitantly lowering the Ce contribution to the magnetic anisotropy. (d) The Kondo effect is strongly sensitive to the local environment: it is dramatically enhanced by nitrogen interstitials thus almost completely suppressing the Ce-4f contribution to the magnetic anisotropy.

with a variational approach to evaluate the magnitude of the Ce single-ion magnetic anisotropy. Our work represents, to the best of our knowledge, the first ab initio evaluation of the magnetic anisotropy in Ce intermetallics explicitly taking into account the impact of the Kondo effect. In contrast to previous zero-temperature DFT calculations, we, in the present study investigates the full temperature dependence of the Ce magnetic anisotropy. Our theoretical predictions are compared to the experimental magnetic anisotropy that we measure, for the first time, in the same wide temperature range.

We focus on the Ce-Fe "1-12" material system which has recently been under scrutiny as a potential hard magnet. Our calculations show a significant reduction of the Ce magnetic moment due to the Kondo effect. This Kondo screening is found to be very sensitive to substitutions and small-atom insertions. In particular, interstitial nitrogen is predicted to completely suppress the Ce contribution to the magnetization and magnetic anisotropy. This behavior is in drastic contrast to the one observed in "1-12" intermetallics with localized rare-earths, like Nd, where nitrogenation has been found to significantly enhance the uniaxial magnetic anisotropy. Indeed, the unexpected suppression of the Ce magnetization by N interstitials is absent if the Ce moment is treated as purely local and stems from a large enhancement of the Kondo scale by nitrogenation, as schematically shown in Figs. 1b)-d). It is confirmed by our measurements of the anisotropy in polycrystalline samples with and without nitrogenation. Such interstitial atoms effectively controlling the state of the Ce-4f shell could be used for fine-tuning and probing the complex many-electron physics of Ce. Most importantly, our calculations establish the salient fact that even in the absence of Kondo screening the small size of the Ce-4f spin moment necessarily leads to rather small values of the magnetic anisotropy at elevated temperatures. Our study, therefore, reveals significant limitations for the Ce contribution to the magnetic hardness at temperatures relevant for applications.

II. RESULTS

Kondo screening of the Ce magnetic moment in "1-12" systems

The "1-12" Ce-Fe intermetallics crystallize in the tetragonal lattice structure shown in Fig. 1a). A partial substitution of Fe with another transition metal (usually Ti) is necessary to stabilize this "1-12" phase in the bulk. Hence, we consider the realistic CeFe11Ti composition and, for the sake of comparison, also "pure" thermodynamically unstable CeFe12. For the latter we assume the same crystal structure. The magnetic properties of "1-12" rare-earth transition-metal intermetallics can be modified by small-atom interstitials, in particular nitrogen. Nitrogenation has been found to significantly enhance the uniaxial magnetic anisotropy in NdFe12N and NdFe11TiN. Nitrogenated Ce-Fe "1-12" compounds have been patented as prospective high-performance magnets with N interstitials found to significantly increase their Curie temperature and magnetization. Therefore, we also consider nitrogenated CeFe11Ti with N interstitials in the experimentally determined Wyckoff 2b position as shown in Fig. 1a).

The ordered Ce-4f magnetic moment $M_z$ in CeFe12, CeFe11Ti and CeFe11TiN as a function of temperature $T$ is displayed in Fig. 2a) as symbols. This Ce moment is induced by the exchange field $B_{ex}$ generated by the ferromagnetically ordered iron sublattice, as schematically shown in Figs. 1b)-d). In our ab initio approach, abbreviated below as DMFT(QMC), we take into account the magnetization of Fe within the local spin-density approximation (LSDA), while many-electron effects on the Ce-4f shell are treated within Dynamical Mean Field Theory (DMFT) in conjunction with a numerically-exact quantum Monte Carlo (QMC) approach. With the Fe fer-
romagnetism included within LSDA, the exchange field \( B_{ex} \) acting on the Ce-4f shell is virtually temperature-independent. Hence, the \( M_z \) vs. \( T \) curve reflects the temperature-dependence of the Ce-4f magnetic susceptibility. One observes a weak \( T \) dependence for all three compounds; it is very different from a Curie-like behavior expected for Ce-4f local moments subjected to an exchange field. The obtained values are well below the saturated \( M_z \) value of 2 \( \mu_B \) for the Ce \( f^{5/2} \) manifold. In particular, in CeFe\(_{11}\)TiN the 4f moment is tiny (0.04 \( \mu_B \)). A small increase of the Ce-4f magnetic moment with respect to pure CeF\(_{12}\) is induced by Ti substitution. Overall, the magnitude and temperature dependence of the Ce-4f magnetic moment in the investigated "1-12" intermetallics correspond to a Kondo-screened Fermi-liquid Ce-4f state.

For comparison, the ordered Ce-4f magnetic moment \( M_{\text{4f}}^{\text{tot}} \) has also been calculated within a quasi-atomic (Hubbard-I) approximation\(^{23,24}\) to the Ce-4f quantum impurity problem (solid lines in Fig. 2). In this approach, abbreviated below as DFT+HubI, the Kondo-effect is neglected (cf. Fig. 1). The Ce magnetic moment evaluated within DFT+HubI exhibits the expected Curie behavior and is significantly larger than the Kondo-screened one at low temperatures. Above \( T \approx 400 \) K the magnitude of the Ce magnetic moments in CeFe\(_{12}\) and CeFe\(_{11}\)Ti agree reasonably well between DFT+HubI and DMFT(QMC) indicating this temperature to be the Kondo scale of these compounds. Within the quasi-atomic picture one would expect the largest \( M_{\text{4f}}^{\text{tot}} \) for CeFe\(_{11}\)TiN (blue solid line in Fig. 2), for which the DMFT(QMC) moment remains, however, heavily screened in the whole temperature range up to 600 K.

### Magnetic anisotropy of Ce in the quasi-atomic picture

In the quasi-atomic approximation (schematically shown in Fig. 1) the single-ion anisotropy due to the Ce-4f magnetic moments is determined by \( B_{ex} \) stemming from the Fe sublattice and the crystal field (CF) splitting on the Ce-4f shell\(^{29}\). While the magnitude of \( B_{ex} \) is similar in all three investigated compounds, the CF splitting turns out to be very different (see the crystal field parameters \( A_2^0(r^2) \) in Table 1). Of particular interest for the Ce-4f magnetic moment at low temperature is the composition of the ground state levels. The CF ground state in CeFe\(_{11}\)TiN is well separated from excited states and consists almost exclusively of the \( |\pm 5/2\rangle \) eigenstates, which have the largest \( |M_{\text{4f}}^{\text{tot}}| \) among the \( j = 5/2 \) manifold. CeFe\(_{11}\)TiN is thus expected to exhibit a strong easy-axis magnetic anisotropy in the quasi-atomic picture. In CeFe\(_{11}\)Ti the contribution of the \( |\pm 5/2\rangle \) eigenstates to the CF ground state is reduced leading to a smaller easy-axis anisotropy; in CeFe\(_{12}\) the CF ground state is \( |\pm 1/2\rangle \) corresponding to an easy-plane anisotropy (see supplementary material for the full CF levels scheme).

### Table I: Ce-4f magnetic moment \( M_z [\mu_B] \) obtained in DMFT(QMC) at 300 K, as well as the lowest-rank crystal-field parameter \( A_2^0(r^2) [K] \), the exchange field \( B_{ex} \) [Tesla] and the quasi-atomic Ce single-ion anisotropy coefficients \( K_{q}^{\text{tot}} [K] \) at 4.2 and 300 K.

|          | \( M_z \) | \( A_2^0(r^2) \) | \( B_{ex} \) | \( K_{q}^{\text{tot}}(4.2 \text{ K}) \) | \( K_{q}^{\text{tot}}(300 \text{ K}) \) |
|----------|----------|-----------------|-------------|--------------------------------------|--------------------------------------|
| CeFe\(_{12}\) | 0.27    | -58             | 305         | -70.6                                | -2.0                                  |
| CeFe\(_{11}\)Ti | 0.35   | 137             | 320         | 58.6                                 | 4.5                                   |
| CeFe\(_{11}\)TiN | 0.04   | 424             | 220         | 77                                    | 7.6                                   |

We extract the values of the CF parameters as well as \( B_{ex} \) from our \textit{ab initio} DFT+HubI calculations and then evaluate the Ce single-ion anisotropy coefficients. The resulting coefficients \( K_{q}^{\text{tot}} \) (in K per f.u.) are listed in Table 1. At liquid helium temperature, \( K_{q}^{\text{tot}} \) is easy-plane in CeFe\(_{12}\) and easy-axis in CeFe\(_{11}\)Ti and CeFe\(_{11}\)TiN. For \( T = 300 \) K, CeFe\(_{11}\)TiN exhibits a substantially stronger easy-axis anisotropy as compared to CeFe\(_{11}\)Ti due to a larger value of its low-rank "20" crystal-field parameter (see supplementary material for values). Both compounds exhibit a strong reduction of the anisotropy with increasing temperature. The calculated room-temperature anisotropy constants \( K_{q}^{\text{tot}} \) are in very good agreement with the high-\( T \) limit analytical expression from Ref. 25, which reads

\[
K_{q}^{\text{tot}} = -\frac{(J - 1)(2J - 1)(2J + 3)}{20J} \alpha_J A_2^0(r^2) x^2, \tag{1}
\]

with \( x = \frac{2J(g_J - 1)B_{ex}}{k_B T} \), where \( g_J = 6/7 \) is the gyromagnetic ratio for the Ce-4f\(^{3+} \) shell. Using this analytical expression one may understand the very rapid suppression of the Ce single-ion anisotropy apparent in Table 1. The Zeeman energy \( 2J|g_J - 1|B_{ex} \) associated to the exchange field \( B_{ex} \approx 300 \) K gives a characteristic temperature of \( 2J|g_J - 1|B_{ex}/k_B \approx 140 \) K, explaining the rapid suppression of the \( K_{q}^{\text{tot}} \) values with temperature and the small value at room temperature. For comparison, we note that the same simple estimate for Sm\(^{3+} \), with \( g_J = 2/7 \) gives a five times higher characteristic temperature (700 K) resulting in a 25 times slower reduction of \( K_{q}^{\text{tot}} \) vs. \( T \) at high temperatures. Hence, as the small magnitude of the spin represents an intrinsic feature of the Ce\(^{3+} \) ion, i. e. not sensitive to the crystalline environment, the Ce-4f contribution to the magnetic hardness at room temperature and above is also expected to be \textit{intrinsically} weak.

Fig. 2(b) shows our measured anisotropy fields obtained from hard-axis measurements of the textured samples. Our results are consistent with the measurements at room temperature previously reported in Refs. 11, 17 and 18. The anisotropy field is already relatively small at low-temperature, and then exhibits a rather slow decay with temperature.

In order to compare theory and experiment, one needs to add the contribution from the Fe-sublattice to the calculated single-ion \( K_{q}^{\text{tot}} \) of Ce. As in this work we do not aim at calculating the Fe-sublattice magnetic anisotropy,
FIG. 2: Temperature dependence of Ce-4f magnetism in Ce-Fe “1-12”. (a) Calculated temperature-dependence of the Ce-4f magnetic moments \( M_z \) in CeFe\(_{12} \) (black squares), CeFe\(_{11}\)Ti (red circles) and CeFe\(_{11}\)TiN (blue triangles). At low temperatures the Kondo-screened Ce-4f magnetic moments (symbols) are much smaller than their expected quasi-atomic values (solid lines). The Kondo effect is the strongest in CeFe\(_{11}\)TiN. (b) Temperature dependence of the anisotropy field \( H_A \) [Tesla] in CeFe\(_{11}\)Ti (in red) and CeFe\(_{11}\)TiN (in blue). In addition to the theoretical and experimental results obtained in this work, values from Refs. a), 17 b) 18 and c) 4 are shown for comparison.

TABLE II: Anisotropy field \( H_A \) [Tesla] calculated within the quasi-atomic approximation (DFT+HubI) and with the Kondo effect included in DMFT(QMC). Experimental values from Refs. 17, 18 and 4 are indicated by superscripts \(^a\), \(^b\) and \(^c\), respectively.

| T (K) | DFT+HubI | DMFT(QMC) | Experiment |
|-------|-----------|------------|------------|
| CeFe\(_{11}\)Ti | 11.6 | 5.8 | 5.1 |
|       | 1.6 | 1.4 | 2.5 |
|       | 5.1 | 7.0\(^a\) | 2.3\(^a\) |
| CeFe\(_{11}\)TiN | 12.3 | 3.2 | 2.0 |
|       | 2.5 | 3.5\(^b\) | 1.5 \(^b\) |
|       | 4.2\(^a\) | 1.3 |
|       | 2.0 \(^a\) |

we extract its value and temperature-dependence from measurements performed on YFe\(_{11}\)Ti\(^{28}\) using the experimental dependence \( K^{Fe}(T) = 23.3 - 28T/T_c \) [K/f.u.] measured in Ref. 28 together with our measured Curie temperatures. At low \( T \), the iron contribution is much smaller than the Ce one and does not affect the picture qualitatively.

Using the relation \( H_A \approx \frac{2K^{tot}}{M_S} \), where \( H_A \) is the anisotropy field, \( M_S \) the total magnetic moment of the compound saturated in the direction of \( H_A \), and \( K^{tot} = K^{Fe} + K^{at} \), we calculate the corresponding values of \( H_A \) in the quasi-atomic approximation listed in Table II together with the experimental values. The quasi-atomic approximation predicts a strong anisotropy that decreases quickly with temperature, while experimentally one finds only a moderate decrease with \( T \), in particular in CeFe\(_{11}\)TiN, which bears little resemblance to the predictions of DFT+HubI. Notice that the standard DFT calculations of Refs. 15 and 16 treating Ce-4f as delocalized band-like states find almost no difference in the zero-temperature anisotropy of CeFe\(_{11}\)Ti and CeFe\(_{11}\)TiN, also in disagreement with experimental results. Hence, neither DFT nor the quasi-atomic treatment is able to capture the impact of interstitials on the Ce magnetic anisotropy. As we show below, the theoretical picture is drastically modified when the impact of Kondo screening on the Ce-4f magnetic anisotropy is taken into account within a full many-body framework.

### Ce magnetic anisotropy in the presence of Kondo screening

A quantitative evaluation of the magnetic anisotropy of a partially Kondo-screened magnetic moment is a formidable problem which—to the best of our knowledge—has not been addressed even for simple model systems so far. In the context of the present work on complex realistic systems we have developed a variational approach to meet this challenge. In order to capture the interplay of the Kondo interaction \( (H_K) \) with the exchange \( (H_B) \) and crystal \( (H_{CF}) \) fields in the total impurity Hamiltonian \( H = H_K + H_B + H_{CF} \) for the Ce-4f shell we assume the ground state of the Ce-4f shell to be given by the following variational many-electron wave function:

\[
\Psi = \sqrt{1 - \alpha^2} \Psi_S + \alpha \Psi_J,
\]

where \( \Psi_S \) is the singlet formed by the Ce-4f total moment coupled to the conduction-electron sea defined by
FIG. 3: Impact of nitrogenation on electronic correlations and spectral function of CeFe$_{11}$Ti (a) Real part of the self-energy $\Sigma(\omega)$ in CeFe$_{11}$Ti (in red) and CeFe$_{11}$TiN (in blue). The quasiparticle weight $Z$ and Ce-4$f$ shell occupation $n_f$ are also indicated in the corresponding colors. (b) Imaginary part of the hybridization function $\Delta(\omega)$. In particular at the Fermi energy $\text{Im} \Delta(\omega)$ is considerably larger in the nitrogenated compound. (The shown self-energies (a) and hybridization functions (b) are averaged over the six orbital contributions with the largest occupation number, respectively). (c)-(d) Corresponding spectral functions. The Ce-4$f$ Kondo peak at the Fermi energy is more pronounced in CeFe$_{11}$TiN due to the more delocalized character of its Ce-4$f$ electrons. For orientation, also the Fe-3$d$, Ti-3$d$ and N-2$p$ states are shown (the Fe-3$d$ contribution has been rescaled by a factor 1/3).

$H_c$; the second term $\Psi_J$ in Eq. (2) represents the 4$f$ ground state in the absence of Kondo screening, i.e. determined by $H_B + H_{CF}$; $\alpha$ is a variational coefficient. Only the second term, due to its non-zero angular momentum, couples to the exchange field

$$\langle \Psi | H_B + H_{CF} | \Psi \rangle = \alpha^2 \langle \Psi_J | H_B + H_{CF} | \Psi_J \rangle.$$  (3)

As shown in the supplemental material, the lowest-order anisotropy coefficient obtained with the variational ansatz Eq. (2) then reads

$$K_1 = K_{1}^{at} \frac{\alpha^2}{1 + \delta},$$  (4)

where $K_{1}^{at}$ is the anisotropy coefficient in the quasi-atomic approximation (DFT+HubI) as detailed above. The value of $\alpha^2$ is given in accordance with Eq. (3) by $M_x(T = 0)/M^{at}_x(T = 0)$ and can be extracted by extrapolating the curves in Fig. [3a] to zero temperature. The denominator $1 + \delta$ in Eq. (4), where $\delta = K_{1}^{at}/A$, is due to the change of $\alpha$ upon the rotation of $B_{ex}$ from the uniaxial $\vec{B}_{ex} || c$ to in-plane direction and can be evaluated from the dependence of $\alpha^2$ vs. $B_{ex} || z$, calculated by DMFT(QMC) (see supplementary material for details).

By multiplying the quasi-atomic $K_{1}^{at}$ for Ce with the corresponding reduction factors due to the Kondo screening (Eq. [1]) and adding the contribution of the Fe-sublattice $K_{1}^{Fe}(T)$ we obtain the total DMFT(QMC) anisotropy field listed in Table [1]. Strictly speaking, the above variational treatment is applicable only at zero temperature. However, close to room temperature the cerium contribution is overruled by the iron one, and the final value becomes relatively insensitive to the precise estimate of the Kondo reduction factor. At low temperature, instead, the Kondo reduction is very significant and the Ce contribution to $H_A$ is completely suppressed in the nitrogenated compound, but still relatively important in CeFe$_{11}$Ti. The values of the anisotropy field estimated within DMFT(QMC) are in good agreement with our experimental results and previous values reported in Refs. [4] [17] and [18] see Fig. [3b], especially taking into
account uncertainties regarding the Fe contribution. In particular, the dramatic reduction of the anisotropy upon nitrogenation predicted by our calculations is also clearly observed in experiment.

**Electronic structure and Ce-4f hybridization**

As demonstrated above, the magnetic moment and anisotropy of Ce-4f in the CeFe\textsubscript{11}MX intermetallics is heavily influenced by the Kondo effect. Here we analyze its imprint on the electronic structure of CeFe\textsubscript{11}Ti(N) and identify the origin of the enhanced Kondo screening in the nitrogenated system.

In Fig. 3b we show the real part of the DMFT self-energy Re $\Sigma(\omega)$ in CeFe\textsubscript{11}Ti and CeFe\textsubscript{11}TiN, respectively averaged over the six Ce-4f orbital contributions with the largest occupation number. The slope of Re $\Sigma(\omega)$ at $\omega = 0$ is a direct proxy for the strength of electronic correlations and determines the quasiparticle weight: $Z = \left[1 - \frac{d}{d\omega} \text{Re} \Sigma(\omega)|_{\omega=0}\right]^{-1}$. The obtained quasiparticle weight is higher in CeFe\textsubscript{11}TiN, as compared to CeFe\textsubscript{11}Ti, indicating a more delocalized character of the Ce-4f states in the nitrogenated compound. This can also be seen from the low occupation of $n = 0.86$ electrons on the Ce-4f shell in CeFe\textsubscript{11}TiN, deviating stronger from the localized limit with $n = 1$ electron as compared to $n = 0.94$ in CeFe\textsubscript{11}TiN. The DMFT hybridization function shown in Fig. 3b quantifies the hybridization of the Ce-4f shell with other states of the system. Especially at low energies in the vicinity of the Fermi level the hybridization function is much larger in CeFe\textsubscript{11}TiN, indicating an increased mixing of the Ce-4f states with neighboring nitrogen states, e.g. N-2p, which is at the origin of the more delocalized behavior of the Ce-4f electrons.

The corresponding DMFT(QMC) spectral functions are displayed in Figs. 3c)-d). In the characteristic three-peak structure of the Ce-4f spectral function the Kondo peak at the Fermi level is further split into two sub-peaks due to the spin-orbit splitting. The position of the localized features, i.e. the lower and upper Hubbard bands centered at -2 and 5 eV, respectively, is in good agreement with the photoemission (PES) spectra of CeFe\textsubscript{2}\textsubscript{77} (we are not aware of any experimental PES for the CeFe\textsubscript{12} materials family). The more delocalized character of the Ce-4f states in CeFe\textsubscript{11}TiN is also reflected in the spectral function, Fig. 3b): a more prominent Kondo peak and less pronounced Hubbard bands signal a more delocalized behavior.

### III. DISCUSSION

**Implications for the search of cerium-based permanent magnets**

This work introduces a DMFT-based approach to the Ce magnetization and magnetic anisotropy in ferromagnetic intermetallics. We derive a simple formula (Eq. 11) relating the reduction of the magnetic anisotropy due to the Kondo screening with that of the ordered Ce moment; the latter being more easily accessible within DMFT. Moreover, this formula is of general applicability and can be used, for example, to extract the reduction of the anisotropy from the measured Ce magnetization. Our approach quantitatively captures the impact of Kondo screening on the intrinsic magnetic hardness $\kappa$ of realistic Ce systems thus opening the possibility for a theoretical search of Ce-based intermetallics with enhanced $\kappa$.

Our calculations reveal a partially Kondo screened state of the Ce-4f magnetic moment in Ce-Fe intermetallics of the "1-12" family. The Ce-4f localization is found to be particularly sensitive to small-atom interstitials. Nitrogen interstitials strongly enhance the screening of the 4f moment, thus completely suppressing the Ce single-ion contribution to the anisotropy both at liquid helium and room temperature. These theoretical predictions are validated by our experimental measurements finding the anisotropy field in CeFe\textsubscript{11}Ti to be strongly suppressed by nitrogenation, in particular at low temperatures where the Ce contribution is the most significant. This dramatic and unexpected enhancement of the Kondo scale by nitrogen suggests that the state of the Ce-4f shell in hard-magnetic intermetallics can, at low temperatures, effectively be controlled by interstitials.

At the same time, the small magnetic anisotropy of a purely local Ce-4f shell at elevated temperatures found in the present work limits the direct use of cerium-based "1-12" systems as hard-magnetic materials. Cerium can still be successfully used as a partial substitution element for the critical heavy rare-earth elements. In this case the essential magnetic hardness is provided by heavy rare-earths, but their concentration may in some cases be reduced without compromising the magnetic properties as recently shown in Ref. 6 on the example of a mixture of La and Ce reducing the material cost of Nd\textsubscript{2}Fe\textsubscript{14}B-type hard magnetic materials. However, the present study shows that cerium itself should not be expected to provide an essential contribution to the magnetic anisotropy at room temperature and above. This conclusion should be of rather general validity for magnetic Ce intermetallics, unless one finds a—possibly exotic—mechanism allowing the hybridization to enhance the Ce-4f anisotropy in the high-temperature local moment regime (i.e. above the Kondo temperature). Such an enhancement would manifest itself in a larger value of the Ce easy-axis magnetic moment obtained within a full DMFT treatment as compared to the value obtained in the quasi-atomic approximation. In the current "1-12" systems, such an
effect is not observed. Given the environmental and economical impact that is at stake if improved permanent magnet materials are found, it might however be worthwhile to systematically search for it.

IV. METHODS

Theory. Our ab initio calculations—combined DFT and dynamical mean-field theory (DMFT)—describe many-body effects in the Ce-4f shell which take into account on equal footing the key competing energy scales of the problem: the crystal field and exchange field induced by the spin-polarized electronic structure, as well as the spin-orbit coupling. In our spin-polarized DFT+DMFT calculations we take into account the magnetization of Fe within the local spin-density approximation (LSDA), while many-electron effects on the Ce-4f shell are treated with DMFT in conjunction with a numerically-exact quantum Monte Carlo approach (abbreviated as DMFT(QMC)). In the quantum impurity problem we treat all fourteen Ce-4f orbitals as correlated and employ the density-density approximation for the corresponding Coulomb vertex. We calculate the ordered Ce-4f magnetic moment $M_z = \text{Tr} \left[ (\hat{L}_z + 2\hat{S}_z) \rho \right]$ from the converged DMFT density matrix $\rho$. Our DFT+DMFT calculations are carried out using the implementation of Refs. 31–34.

For comparison, we also perform DFT+DMFT calculations employing the quasi-atomic Hubbard-I approximation to the Ce-4f quantum impurity problem (DFT+HubI). This approach provides reliable crystal fields and exchange fields in hard-magnetic intermetallics, as previously demonstrated in Ref. 13. Please refer to the supplemental material for further details regarding our ab initio calculations.

The Ce single-ion anisotropy coefficient within the atomic approximation, $K_{1s}^\text{at}$, is evaluated from the dependence of the anisotropy energy $E_{\text{an}}^\text{at}$ on the azimuthal angle $\theta$ of the exchange field $B_{\text{ex}}$ by fitting it to the form $E_{\text{an}}^\text{at} = K_{1s}^\text{at} \sin^2 \theta$. The dependence $E_{\text{an}}^\text{at}$ on $\theta$ is calculated by a numerical diagonalization of the Ce-4f crystal field Hamiltonian under $B_{\text{ex}}$ applied in the corresponding direction, see supplementary material for details.

Experiment. Polycrystalline CeFe$_{11}$Ti samples are produced by the suction casting method using commercial purity elements (> 99.99%). The as-cast samples are wrapped in Mo foil, sealed in a quartz ampule under argon atmosphere and annealed at 850°C for 12 hours followed by quenching in water. Part of the suction-cast plates are ground into powder below 20 µm to carry out the nitrogenation. The determination of the crystal structures is done using a room temperature x-ray powder diffractometer (XRD) and the XRD patterns are fitted with a ThMn$_{12}$-type ($I4/mmm$, space group no. 139) structure. Thermomagnetic measurements are carried out for the determination of the Curie temperatures. The anisotropy fields are measured on the polycrystalline CeFe$_{11}$Ti and CeFe$_{11}$TiN samples by using the method suggested by Durst and Kronmüller. Applications of this model to ThMn$_{12}$-systems have been reported recently for similar material systems. Further details of the sample production and characterization can be found in the supplemental material.

V. DATA AVAILABILITY

The data generated and analyzed during this study are available from the corresponding author upon reasonable request.

1. O. Gutliefisch, M. A. Willard, E. Brück, C. H. Chen, S. G. Sankar, and J. P. Liu, “Magnetic materials and devices for the 21st century: Stronger, lighter, and more energy efficient,” Advanced Materials 23, 821–842 (2011).
2. K. Skokov and O. Gutliefisch, “Heavy rare earth free, free rare earth and rare earth free magnets - vision and reality,” Scripta Materialia 154, 289 – 294 (2018).
3. M. Richter, “Band structure theory of magnetism in 3d-4f compounds,” Journal of Physics D: Applied Physics 31, 1017–1048 (1998).
4. C. Zhou, F. E. Pinkerton, and J. F. Herbst, “Magnetic properties of CeFe$_{11-x}$Co$_x$Ti with ThMn$_{12}$ structure,” Journal of Applied Physics 115, 17C716 (2014).
5. C. Zhou, F. Pinkerton, and J. Herbst, “Cerium-iron-based magnetic compounds,” (2013), US Patent 9,548,150 B2.
6. “Toyota develops new magnet for electric motors aiming to reduce use of critical rare-earth element by up to 50%,” https://newsroom.toyota.eu/ (2018), Accessed: 2019-07-21.
7. H. i. d. I. Sözen, S. Ener, F. Maccari, K. P. Skokov, O. Gutliefisch, F. Körmann, J. Neugebauer, and T. Hickel, “Ab initio phase stabilities of ce-based hard magnetic materials and comparison with experimental phase diagrams,” Phys. Rev. Materials 3, 084407 (2019).
8. Q. Si and S. Paschen, “Front cover: Quantum phase transitions in heavy fermion metals and kondo insulators,” physica status solidi (b) 250, 425–438 (2013).
9. M. Bartashevich, T. Goto, R. Radwanski, and A. Korylov, “Magnetic anisotropy and high-field magnetization process of CeCo$_5$,” Journal of Magnetism and Magnetic Materials 131, 61 – 66 (1994).
10. T. W. Capehart, R. K. Mishra, G. P. Meisner, C. D. Fuerst, and J. F. Herbst, “Steric variation of the cerium valence in CeFe$_{14}$B and related compounds,” Applied Physics Letters 63, 3642–3644 (1993).
11. J. F. Herbst, “R$_2$Fe$_{14}$B materials: Intrinsic properties and technological aspects,” Rev. Mod. Phys. 63, 819–898 (1991).
W. Körner, G. Krügel, and C. Elsässer, “Theoretical
14
P. Delange, S. Biermann, T. Miyake, and L. Pourovskii,
L. Ke and D. D. Johnson, “Intrinsic magnetic properties in
R. Martinez-Casado, A. Dasmahapatra, M. F. Sgroi,
Y. Harashima, K. Terakura, H. Kino, S. Ishibashi, and
M. Akayama, H. Fujii, K. Yamamoto, and K. Tatami,
Q. Pan, Z.-X. Liu, and Y.-C. Yang, “Structural and mag-
A. I. Lichtenstein and M. I. Katsnelson, “Ab initio calcula-
J. Hubbard, “Electron correlations in narrow energy
E. Gull, A. J. Millis, A. I. Lichtenstein, A. N. Rubtsov,
M. Kuz’min and A. Tishin, “Theory of crystal-field effects
M. Aichhorn, L. Pourovskii, V. Vildosola, M. Ferrero,
O. Parcollet, T. Miyake, A. Georges, and S. Biermann,
M. Aichhorn, L. Pourovskii, and A. Georges, “Impor-
M. Aichhorn, L. Pourovskii, V. Vildosola, M. Ferrero,
O. Parcollet, M. Ferrero, T. Ayralt, H. Hafermann,
O. Parcollet, M. Ferrero, T. Ayralt, H. Hafermann,
K.-D. Durst and H. Kronmüller, “Determination of in-
V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O.
A. Georgiev, “Strongly correlated electron materials: Dy-
V. I. Anisimov, A. I. Poteryaev, M. A. Korotin, A. O.

VI. ACKNOWLEDGMENTS

We thank Tilmann Hickel, Takashi Miyake, and Halil Sözen for fruitful discussions. This work was supported by the Deutsche Forschungsgemeinschaft and French Agence Nationale de la Recherche in the framework of the international collaborative DFG-ANR project REMAP (Project No. 316912154), the European Research Council under its Consolidator Grant scheme (Project No. 617196) and IDRIS/GENCI Orsay under Project No. 12019091393. A.G. acknowledges support through Schrödinger fellowship J-4267 of the Austrian Science Fund (FWF). L.P. acknowledges computational resources provided by the Swedish National Infrastructure for Computing (SNIC). We thank the computer team at CPHT for support.
VII. AUTHOR CONTRIBUTIONS

A.G. performed the electronic structure calculations, L.P. did the analytical derivations; S.E., F.M., I.D. and K.S. performed the experiments. L.P., S.B. and O.G. led the project. A.G., L.P. and S.E. drafted the manuscript. All authors discussed the results and contributed to the final version of the manuscript.

VIII. COMPETING INTERESTS

The authors declare no competing interests.