Doped SmFe$_{12}$ for permanent-magnet utility: 

*ab initio* material design integrated with experimental characterization

Munehisa Matsumoto\textsuperscript{1}, Takafumi Hawai\textsuperscript{1,2}, Kanta Ono\textsuperscript{1,2,3}  
\textsuperscript{1}Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Oho 1-1, Tsukuba, Ibaraki 305-0801, Japan  
\textsuperscript{2}Elements Strategy Initiative Center for Magnetic Materials (ESICMM), National Institute for Materials Science (NIMS), Sengen 1-2-1, Tsukuba 305-0047, Japan  
\textsuperscript{3}Center for Materials Research by Information Integration (CMI2), Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science (NIMS), Sengen 1-2-1, Tsukuba 305-0047, Japan  
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Past five years have seen a lot of resurgent interests in ferromagnets with the ThMn$_{12}$ crystal structure in the developments for rare-earth permanent magnets (REPM's). It has been shown both theoretically and experimentally that the intrinsic magnetism of Sm(Fe,Co)$_{12}$ and NdFe$_{12}$N$_x$ may potentially be superior to Nd$_2$Fe$_{14}$B if the bulk structure stability is guaranteed, which is so far achieved only on a special substrate in laboratory. Bulk structure stability is achieved by the presence of the third dopant element as is the case with SmFe$_{11}$Ti. It is now in high demand to find out with which chemical composition a good compromise in the trade-off between structure stability and strong ferromagnetism is reached. We inspect the effects of representative dopant elements, Zr, Ti, and Co in SmFe$_{12}$ from first principles to track the trend in formation energy and intrinsic magnetism as a function of dopant concentration. Combining *ab initio* data with experimental data from neutron scattering, we determine the internal coordinates of dopants elements and Fe atoms, lattice constants, and magnetic moments on each site in the multiple-sublattice structure of ThMn$_{12}$-type crystal in a self-consistent way. Utility of Zr and Ce, in an analogous way to Co, is discussed as an effective doping of extra electrons.

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*Introduction*  
Rare-earth permanent magnet (REPM) based on Nd$_2$Fe$_{14}$B \cite{1-4} have been in commercial use in the past several decades. Nd-Fe-B ternary alloys based on R$_2$Fe$_{14}$B (R=rare earth including Nd) make excellent permanent magnets except for a caveat on relatively low Curie temperature: the Curie temperature of Nd$_2$Fe$_{14}$B is 585 K, which is only marginally beyond the typical high-temperature edge at 450 K of practical use in traction motors and power generators. Thus a way to supplement the high-temperature properties has been pursued in various respects, most notably addition of heavy-rare-earth elements to help high-temperature coercivity via enhancing the high-temperature anisotropy field. Along the line of searches for alternative materials with higher Curie temperature or/and improved temperature coefficient of magnetization and anisotropy field, NdFe$_{12}$N \cite{5-7} and Sm(Fe,Co)$_{12}$ \cite{8} recently have triggered renewed interest in ferromagnets with the ThMn$_{12}$-type crystal structure as shown in Fig. 1. Originally it was only a few years after the discovery of Nd$_2$Fe$_{14}$B that the material based on the ThMn$_{12}$ crystal structure had been found \cite{9}, but the drawback that the particular ThMn$_{12}$ crystal structure is only metastable for RFe$_{12}$ (R=Nd, Sm, and other rare earth) had hindered further developments. The problem is not yet entirely eliminated even now \cite{10}, but persistent efforts to bring the structure stability closer \cite{11,12} and recent renewed efforts \cite{13-18} together with the advent of various ways of data exploitation may change the perspective. This work presents an attempt to combine theoretical and experimental data to work with the severe trade-off that is almost always encountered among the prerequisites for a ferromagnet to make a good main phase of REPM, namely, strong magnetization, accordingly strong uniaxial magnetic anisotropy, high Curie temperature, and good structure stability, for the particular case of doped SmFe$_{12}$.

*Methods and target materials*  
Effects of dopant elements, Zr, Ti, and Co on pristine SmFe$_{12}$ are investigated by calculating the formation energy and intrinsic

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**Fig. 1.** (Color online) Crystal structure of SmFe$_{12}$. Large and red balls represent Sm(2a) sites and green/cyan/blue and small balls represent Fe(8i)/Fe(8j)/Fe(8f) sites, respectively. In the tetragonal box shown here, two formula units are included.
which is known to predict reasonable lattice parameters based on generalized gradient approximation (GGA) [19], these are plugged into ab initio calculations using co-

FIG. 2. (Color online) Calculated formation energy of doped SmFe_{12}. In the tetragonal unit shown in Fig. 1 containing two formula units of SmFe_{12}, one dopant atom, either Ti, Co, or Zr, replaces one host atom and ab initio structure optimization is done to extract the formation energy.

| Dopant site | Cl pristine SmFe_{12} | FE(8i) | FE(8j) | FE(8k) | RE(2a) |
|-------------|-----------------------|--------|--------|--------|--------|
| ΔE [eV/(f.u.)] | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |

TABLE I. Our ab initio lattice parameters from structure optimization for the pristine material SmFe_{12}, compared to a few previous works [8, 20], and our lattice parameters for doped SmFe_{12} (Zr-doped Sm(Fe,Co,Ti)_{12}) derived from the self-consistent analysis between ab initio calculations and Rietveld analysis of neutron scattering data.

magnetic properties from first principles. Formation energy is obtained through ab initio structure optimization based on generalized gradient approximation (GGA) [19], which is known to predict reasonable lattice parameters for most of the Fe-based ferromagnets. Lattice parameters out of the structure optimization for SmFe_{12} is summarized in Table I together with counterpart numbers from previous theoretical [20] and experimental [8] works. Calculated energy of doped SmFe_{12} is subtracted by with the summation of calculated total energy of the ingredient elements and we inspect how much formation energy is gained by the dopant elements. Details of these ab initio calculations are given in Supplementary Material [21].

As has been shown in Fig. 1 the crystal structure of SmFe_{12} is characterized by multiple sublattices, namely, Sm(2a), Fe(8i), Fe(8j), and Fe(8k). Ab initio studies showed the relative trends in magnetic moment $m[r]$ on site $r$ as $m[Fe(8i)] > m[Fe(8j)] > m[Fe(8k)]$ in RFe_{12} [3]. A guiding principle for the possible design of an optimal material would be to keep the magnetization from Fe(8i) as much as possible while gaining structure stability, but unfortunately the preference of the doped Ti atom goes for the Fe(8i) site from $T = 0$ all the way to higher temperatures [22], which we also confirm for $T = 0$ as shown in Fig. 2. Thus the dominant magnetic moment from Fe(8i) is sacrificed while achieving the bulk structure stability. Given this trade-off, control of the chemical composition toward a better compromise has been pursued in the following way [11, 12]: the structure stability can be gained by Zr partly replacing Sm(2a) and thus the amount of Ti to stabilize the crystal structure might be able to be reduced, leading to an improved magnetization. Now a question can arise concerning the nature of dopant Zr, which should be chemically similar to Ti, being on the same family on the periodic table of elements: how can the preference of host sublattice be so drastically different between Ti and Zr? Indeed our calculations of formation energy of Zr-doped SmFe_{12}, exploring all possible sublattices for the doped Zr atom, show that Zr energetically favors Fe(8i) site as well as Sm(2a) site as shown in Fig. 2. In contrast, recent investigations on (Sm,Zr)(Fe,Co,Ti)_{12} are in progress presuming that Zr atom mostly replaces Sm(2a) [17]. Precise understanding on the roles of Zr in Sm(Fe,Co,Ti)_{12} seems to be in acute need.

In order to take a closer look into the experimental facts for Zr-doped SmFe_{12}, we combine ab initio inputs and outputs with our experimental data from magnetic neutron scattering. Here the powder sample of Sm_{0.8}Zr_{0.2}(Fe_{0.7}Co_{0.3})_{11.25}Ti_{0.75} was provided by Toyota Motor Corporation and the powder neutron diffraction measurements at room temperature were performed on ECHIDNA at Australian Nuclear Science and Technology Organisation (ANSTO) [23]. Rietveld analysis of diffraction data [24] gives the lattice constants and the internal coordinates of Fe(8i) and Fe(8j) in the unit cell. These are plugged into ab initio calculations using coherent potential approximation (CPA) [25] based on local density approximation (LDA) following Vosko, Wilk, and Nusair [26] which is known to give reasonable magnetic moments on a given crystal structure. We make a few steps further: calculated magnetic moment on each atom is fed back into the Rietveld analysis of diffraction data to obtain the refined input data consisting of lattice constants and internal coordinates [27]. We observe that this overall self-consistent iteration loop between Rietveld-analysis of experimental data ab initio calculations converges in quite a fast and robust way. We would tentatively refer to this particular combination of theory and experiment as “LDA+Rietveld”. Detaile data during the overall iteration procedure can be found in the supplementary information [21]. Combination of the Rietveld analysis with ab initio calculation...
to verify the structure stability has been widely done recently [28], while the way to reinforce the convergence of the data via the feedback between theory and experiment is new to the best of the authors’ knowledge. Here the scope of the problem imposed on the Rietveld analysis is slightly different from the conventional one for the structure analysis: out lattice structure space is limited, restricting ourselves on the given prototype of ThMn$_{12}$ structure analysis: out lattice structure space is limited, while the details of the sublattice-resolution in the multiple-sublattice ferromagnetism is the present problem. In such a restricted working space, the feedback between theory and experiment can be implemented directly and easily.

For the assessment of magnetic anisotropy in the typical working temperature range, one of the most influential factors is actually an indirect exchange coupling between rare earth atom and Fe atom [29]. We use Sm(5d)-Fe(3d) exchange coupling as a key descriptor for the anisotropy field which intrinsically controls the coercivity. Thus we actually do without spin-orbit interaction in our ab initio calculations. Even though we do not directly address the uni-axial magnetic anisotropy, inspection of linear trends in the leading order contribution around a reasonable limit at the pristine SmFe$_{12}$ would do. This simplifies the theory part and enable a wide coverage of parameter space spanned by the chemical composition. Our target observables consist of the formation energy, magnetization, and inter-atomic exchange couplings out of which Fe-Fe couplings control the Curie temperature and Fe-Sm couplings control the room-temperature anisotropy field.

**Calculated formation energy of doped SmFe$_{12}$** We inspect the influence of each dopant element, Ti, Co, and Zr, in SmFe$_{12}$ on the structure stability based on the derivative of calculated formation energy $\Delta E$ with respect to the concentration of dopant elements and see how the amount of Ti can be reduced with the possible help from Zr and Co to be on a par with SmFe$_{11}$Ti concerning the structure stability. Negative and large absolute value of the formation energy is beneficial. The exact formula and values of calculated energy are summarized in the Supplemental Material [21]. The results for doped SmFe$_{12}$ have been shown in Fig. 3. Observing the minimum energy among the multiple choices for the dopant elements, the preference of doped Ti goes for Fe(8i), Co does for Fe(8f), both in agreement with the claims of past works, while the conclusion for Zr is not clear from this data set: Zr in Fe(8i) and Zr in Sm(2a) look almost degenerate energetically. Formation energy is summarized as a function of concentration as shown in Fig. 3. Utility of a dopant element M may be characterized by a differential coefficient, $(-\partial \Delta E/\partial c_M)$, where $c_M$ is the concentration of M. From the data shown in Fig. 3 the coefficients are extracted as shown in Table II. Ti indeed works for the structure stability most effectively. For our target compound (Sm$_{1-x}$Zr$_x$)(Fe$_{1-y}$Co$_y$Co$_y$Zr$_{xt}$)$_{12}$ to be better or on a par with SmFe$_{11}$Ti concerning the formation energy, the following relation must be met

\[
xU_{\Delta E}(Zr(2a)) + yU_{\Delta E}(Co) + zU_{\Delta E}(Ti) + z'U_{\Delta E}(Zr(8i)) \cong (1/12)U_{\Delta E}(Ti)
\]

Assuming uniform substitution by Co considering the relatively minor preference of Co doped in SmFe$_{12}$, the following relation is imposed.

\[
0.63x + 1.11y + 13.6z + 7.4z' \cong 1.133
\]  

(1)

With our sample $(x,y) \simeq (0.2, 0.3)$, we end up with the relation $z + 0.54z' \cong 0.05$. So $z \cong 0.05$ if $z' = 0$ and possibly a few percent of $z'$ further reduces $z$. Thus the lower bound can be smaller than $z = 1/12 = 0.083$ in SmFe$_{11}$Ti by 40%. We quantitatively confirm that Zr in Sm(2a), partly also in Fe(8i), and uniformly doped Co indeed enables the reduction of Ti concerning the formation energy.

| dopant | $U_{\Delta E} \equiv (-\partial \Delta E/\partial c(M))$ [eV/(formula unit)] |
|---------|---------------------------------------------------|
| Zr in Sm(2a) | 0.63 |
| Zr in Fe(8i) | 7.4 |
| Ti in Fe(8i) | 13.6 |
| Co (uniformly doped) | 1.11 |
| Co in Fe(8f) | 4.8 |

**TABLE II.** Derivative of the formation energy of doped SmFe$_{12}$ around the pristine limit with respect the concentration of dopant elements.
LDA+Rietveld results for Zr-doped Sm(Fe,Co,Ti)\textsubscript{12}

Having confirmed the assumed utility of Zr for the structure stability from first principles, we inspect the real sample of Sm\textsubscript{0.8}Zr\textsubscript{0.2}(Fe\textsubscript{0.7}Co\textsubscript{0.3})\textsubscript{11.25}Ti\textsubscript{0.75} to see how the calculated site preference may be reflected in experimental reality. Rietveld analysis is performed to extract the localized magnetic moments, concentration distribution of component elements occupying the same sublattice, internal coordinates, and lattice constants. Out of these outputs from the experimental data analysis, the lattice structure information typically make the inputs to \textit{ab initio} calculations in order to do the simulations of the complicated multiple-sublattice material as realistically as possible. \textit{Ab initio} structure optimization does illustrate the relative trends but it does not always pin-point the quantitative results from experimental measurements, as is seen in Table I. Detailed and reliable inputs for the internal coordinates as well as the lattice constants, such as reported in Ref. \textsuperscript{30} for YFe\textsubscript{2}Ti, have been in great demand to address the subtle interplay among various contributions from different sublattices and the trade-off between prerequisite properties for multiple-sublattice magnets.

Given the structural inputs, \textit{ab initio} calculations yield electronic structure including magnetic moment on each atom: these outputs can now be recycled as a renewed input to the Rietveld analysis so that the solution of the inverse problem to decode the neutron diffraction pattern would be more robust \textsuperscript{27}. We have iterated such feedback process from \textit{ab initio} outputs to Rietveld analysis in the next step until self-consistency is reached, now following Korringa-Kohn-Rostoker (KKR) Green’s function method combined with coherent potential approximation (CPA) for alloys \textsuperscript{25}. The details of the computational setup and the specific way the overall iteration proceeds are described in the Supplemental Material \textsuperscript{21}. Remarkably, the convergence down to 5-6 digits is achieved within a few iteration steps, counting a set of Rietveld analysis and \textit{ab initio} calculation as one step. We observe that either case of Sm\textsubscript{2}a taking Zr or Fe\textsubscript{8i} taking Zr is equally plausible, in line with the site preference inspected with the \textit{ab initio} structure optimization. The resultant lattice constants have been summarized in Table I. The detailed quantitative distribution of Zr over Sm\textsubscript{2}a and Fe\textsubscript{8i} has not been entirely determined here due to a problem with Zr in the Rietveld analysis of the neutron scattering data in that magnetic moment on Zr may be too small. At least we have seen that there should be some finite contribution from some Zr atoms doped into the Fe\textsubscript{8i} sublattice.

Optimal chemical composition for the doped SmFe\textsubscript{12} Now the prerequisite magnetic properties for REPM are inspected. The observables are magnetization, Curie temperature as obtained on the basis of mean-field approximation for calculated exchange couplings between \textit{d}-electrons, and the 5\textit{d}-3\textit{d} exchange couplings that indirectly binds \textit{f} and 3\textit{d} electrons together as a key measure for finite-temperature magnetic anisotropy \textsuperscript{29}. The last observable is denoted as “\textit{J}_{\text{RT}}\textsuperscript{Curie}”, emphasizing that this is the coupling between rare-earth atom (R) and transition-metal atom (T). For SmFe\textsubscript{12}, there are three sublattices for Fe and accordingly \textit{J}_{\text{RT}}\textsuperscript{Curie} has three variants \textit{J}_{\text{RT}}\textsuperscript{Curie}(8\textit{i}), \textit{J}_{\text{RT}}\textsuperscript{Curie}(8\textit{j}), and \textit{J}_{\text{RT}}\textsuperscript{Curie}(8\textit{f}). Calculated results of them for doped SmFe\textsubscript{12}, here we denote as Sm\textsubscript{1−\textit{z}}Zr\textsubscript{\textit{z}}(Fe\textsubscript{1−\textit{y}}−\textit{z},\textit{z})Co\textsubscript{\textit{y}}Ti\textsubscript{\textit{z}}Zr\textsubscript{\textit{z}′} for each of the focus elements: Ti, Co, and Zr, are shown in the Supplemental Material \textsuperscript{21}.

The partial derivative coefficients of the target observables \textit{M}, \textit{T}_{\text{Curie}}, \textit{J}_{\text{RT}}\textsuperscript{Curie} for Fe\textsubscript{8i}, Fe\textsubscript{8j}, and Fe\textsubscript{8f}, with respect to \textit{x}, \textit{y}, \textit{z}, and \textit{z}′ around the pristine limit, SmFe\textsubscript{12} \textsuperscript{20}, can be summarized as follows. The detailed derivation of this working matrix is given in the Supplemental Material \textsuperscript{21}.

\[
\begin{pmatrix}
\frac{\partial M}{\partial x}/M & \frac{\partial M}{\partial y}/M & \frac{\partial M}{\partial z}/M & \frac{\partial M}{\partial z′}/M \\
\frac{\partial T_{\text{Curie}}/\partial x}/T_{\text{Curie}} & \frac{\partial T_{\text{Curie}}/\partial y}/T_{\text{Curie}} & \frac{\partial T_{\text{Curie}}/\partial z}/T_{\text{Curie}} & \frac{\partial T_{\text{Curie}}/\partial z′}/T_{\text{Curie}} \\
\frac{\partial J_{\text{RT}}(8\textit{i})/\partial x}/J_{\text{RT}}(8\textit{i}) & \frac{\partial J_{\text{RT}}(8\textit{i})/\partial y}/J_{\text{RT}}(8\textit{i}) & \frac{\partial J_{\text{RT}}(8\textit{i})/\partial z}/J_{\text{RT}}(8\textit{i}) & \frac{\partial J_{\text{RT}}(8\textit{i})/\partial z′}/J_{\text{RT}}(8\textit{i}) \\
\frac{\partial J_{\text{RT}}(8\textit{j})/\partial x}/J_{\text{RT}}(8\textit{j}) & \frac{\partial J_{\text{RT}}(8\textit{j})/\partial y}/J_{\text{RT}}(8\textit{j}) & \frac{\partial J_{\text{RT}}(8\textit{j})/\partial z}/J_{\text{RT}}(8\textit{j}) & \frac{\partial J_{\text{RT}}(8\textit{j})/\partial z′}/J_{\text{RT}}(8\textit{j}) \\
\frac{\partial J_{\text{RT}}(8\textit{f})/\partial x}/J_{\text{RT}}(8\textit{f}) & \frac{\partial J_{\text{RT}}(8\textit{f})/\partial y}/J_{\text{RT}}(8\textit{f}) & \frac{\partial J_{\text{RT}}(8\textit{f})/\partial z}/J_{\text{RT}}(8\textit{f}) & \frac{\partial J_{\text{RT}}(8\textit{f})/\partial z′}/J_{\text{RT}}(8\textit{f})
\end{pmatrix}
\]

\[
\begin{pmatrix}
0.0244238 & 0.363045 & -0.757551 & -0.709945 \\
0.196759 & 2.8095 & -0.0191428 & -0.278903 \\
0.0955673 & 0.997759 & -0.192314 & -0.370551 \\
0.116806 & 0.965723 & 0.321699 & 0.134062 \\
0.135327 & 0.736807 & -0.145208 & -0.199097
\end{pmatrix}
\]

Each element in the above derivative matrix has been normalized by the absolute values at the pristine limit.

It is up to a user of the material how those prerequisite properties are to be prioritized. If we plainly
optimize the overall improvement ratio as defined by \( (\partial O/\partial c)/c|_{c=0} \) where \( O = M \), \( T_{\text{Curie}} \), or \( J_{\text{RT}} \) is the target observable and \( c = x, y, z, \) or \( z' \) is the concentration of the dopant elements, \( \sum c (\partial O/\partial c)/c|_{c=0} \) under the stability condition as given by Eq. (1), we end up with a problem to maximize an overall merit function \( U = 0.569x + 5.87y - 0.793z - 1.42z' \). We note that the expansion around the pristine limit should be used only within the linear regime, \( 0 \leq x, y, z, z' \leq 0.2 \) referring to the calculated observables in the Supplemental Material [21]. The extra presence of Zr in Fe(8i) site is hardly beneficial and presence of Ti in Fe(8i) seems to help in largely eliminating this possibility. If we neglect the contribution from \( z' \) and focus on the minimization of \( z \), going up to the limit of the linear regime in \( x \) and \( y \) to 0.2 and the lower limit of \( z \) is identified to be 0.058, which amounts to 0.7 Ti atom per SmFe\(_{12}\). This seems to be the best compromise starting from a pristine limit of SmFe\(_{12}\). In our experimental sample, 30% of Co might be overkilling the structure stability problem by sacrificing a part of magnetization and possibly also the anisotropy field, which might be effectively compensated in the room-temperature observation through the persistent enhancement Curie temperature beyond the assumed linear regime for most of the other observables.

**Discussions** It is noted in the trend of the calculated observables in SmFe\(_{12}\) doped with Ti, Co, and Zr that Zr(2a) actually helps in enhancing magnetization and others, instead of diluting the magnetic properties of pristine SmFe\(_{12}\), within the approximation of the fixed lattice. This can be understood as an electron-doping effect into the \( d \)-electron band in an analogous way to the Slater-Pauling curve where Co adds up one electron on top of \( 3d \)-electron band of Fe to maximize the magnetization [31, 32]. The magnetic equivalent of Zr to Co is measured by a rescaling 12\(z \times y \) as can be inspected in Fig. 4. The same effect can be realized with Ce\(^{4+}\) doped into Sm(2a) site as overlapped on top of Zr-doped case and Co-doped case. Here a part of the delocalized \( 4f \)-electrons, which seems to be 80% as inspected from a manual scaling to achieve the data collapse seen in Fig. 4, hybridizes with \( d \)-electron band and adds up the filling, leading to an analogue of the Slater-Pauling curve in the particular electronic structure of 4f-3d intermetallics.

Doped Ce\(^{4+}\)-supplying extra electrons in the host system is apparently analogous to electron-doped cuprates [33, 34]. While the nature of the host system, which here is a metal that is not so good in terms of electric conduction, resides on the opposite side of the presumed Mott insulator for cuprates, doping seems to work on the localized part of the electronic state that is actually common between our 4f-3d intermetallic ferromagnets and doped Mott insulators [35]. As seen in the Supplemental Material [21], Zr(2a)-induced enhancement of magnetization and the same effect from Ce\(^{4+}\) mostly happens in the Fe(8f) sublattice, which resides in the immediate neighborhood of the Sm(2a) sublattice. Understanding and control of such local mechanism in the real space should help in implementing fortunate cases like Zr-doped SmFe\(_{12}\) [18], where both magnetic ferromagnetism and structure stability can be gained at the same time.

**Conclusions and outlook** We have inspected an optimal chemical composition for a ferromagnet SmFe\(_{12}\) presuming the possible utility as a permanent magnet. Representative dopants, Ti, Co, Zr have been considered. Combining experimental data and \textit{ab initio} data in a self-consistent way, we have seen that, in Zr-doped SmFe\(_{12}\), Zr occupies both Sm(2a) and Fe(8i) almost equally likely in terms of energetics. While Ti as the stabilization element has been found to be unavoidable, the lower bound found \textit{ab initio} around 0.7 is close to what has been achieved experimentally so far [17]. Concerning the intrinsic magnetization enhanced by Zr [18], we find that the electron doping effects brought by Zr can be exploited to gain both of structure stability and magnetization. The similar effect is expected for Ce as well. Both of these happens because of the particular electronic structure with the hybridization between 3d-electron band from the Fe sublattices and 5d-electron band from rare earth sublattice. The localized component in the electronic structure of doped SmFe\(_{12}\) with the dual nature of localization and delocalization seems to show an analogous physics to electron-doped cuprates, even if the host system resides on the opposite sides sandwiching a virtual metal-insulator transition [36].

Methodologically, the construction to iterate between macroscopically measured experimental data and microscopically calculated \textit{ab initio} data might make a step forward to a multi-scale description of materials, which
should be an important part of the possible theoretical description of coercivity of REPM’s.

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the sum of the energy of the constitute elemental systems as follows:

and compare the relative trends among them concerning magnetization and the energy of the electronic state.

optimized lattice parameters for each of (Sm,Zr)Fe$_{24}$

experimental work on NdFe$_{12}$

the total energy of the electronic state with the given chemical composition. For Zr-doped SmFe$_{24}$

and 24 Fe atoms, are replaced by impurity atoms one by one, and the crystal lattice structure is optimized to evaluate

starting structure parameters, one of the host atoms in the tetragonal unit, with two formula units i.e. two Sm atoms

of starting internal coordinates, (x$_5$

the internal coordinates as imposed by the local hexagonal symmetry of the CaCu$_3$.

on the side faces of the tetragonal box shown in Fig. 1 of the main text. There is a relation 2(0

ab initio type of calculations, OpenMX [S1–S6] which works on the basis of pseudopotentials [S7, S8] and localized basis sets. Present

The choice of the local basis set has been the followings:

systems have been described elsewhere [S9]. We concisely describe what is extensively used in the present study.

as Sm(2$_5$

and Fe(8$_8$

has been defined up to the particular choice of the basis sets and the pseudopotentials specified above and it is not entirely the true total energy.

In the lattice structure of SmFe$_{12}$ shown in Fig. 1 in the main text, there are three sublattices for Fe, namely, Fe(8$_i$), Fe(8$_j$), and Fe(8$_f$), and one rare-earth sublattice, Sm(2$_a$). The internal cartesian coordinates of them can be defined as Sm(2$\alpha$)(0,0,0), Fe(8$_i$)(x$_i$, 0, 0), Fe(8$_j$)(x$_j$, 0.5, 0), and Fe(8$_f$)(0.5 – x$_j$, 0, 0.5). It is instructive to note that Fe(8$_i$) and Fe(8$_j$) atoms approximately form a regular hexagon, corresponding to Co(2$c$) atoms in the SmCo$_5$ prototype [S11] on the side faces of the tetragonal box shown in Fig. 1 of the main text. There is a relation 2(0.5 – x$_j$) ≃ x$_j$ among the internal coordinates as imposed by the local hexagonal symmetry of the CaCu$_3$ prototype. We typically set a set of starting internal coordinates, (x$_{5i}$, x$_{5j}$) = (0.36, 0.27) which roughly satisfies this relation. Referring to the recent experimental work on NdFe$_{12}$ [S12] we set a set of starting lattice constants to be (a, c) = (8.52, 4.80) [Å]. With these starting structure parameters, one of the host atoms in the tetragonal unit, with two formula units i.e. two Sm atoms and 24 Fe atoms, are replaced by impurity atoms one by one, and the crystal lattice structure is optimized to evaluate the total energy of the electronic state with the given chemical composition. For Zr-doped SmFe$_{12}$, we obtain the optimized lattice parameters for each of (Sm,Zr)Fe$_{24}$ and Sm$_2$Fe$_{23}$Zr on the tetragonal unit with two formula units and compare the relative trends among them concerning magnetization and the energy of the electronic state.

The formation energy ∆E[C] of a compound C is defined as a difference between the energy of the compound and the sum of the energy of the constituent elemental systems as follows:

\[
\Delta E_{\text{form}}[\text{Sm}_1-x\text{Zr}_x(\text{Fe}_{1-y-z}\text{Co}_y\text{Ti}_z)_{12}] = U_{\text{tot}}[\text{Sm}_1-x\text{Zr}_x(\text{Fe}_{1-y-z}\text{Co}_y\text{Ti}_z)_{12}] - (1-x) \frac{U_{\text{tot}}[\alpha-\text{Sm}]}{N_{\text{atom}}[\alpha-\text{Sm}]} - x \frac{U_{\text{tot}}[\text{hcp-Zr}]}{N_{\text{atom}}[\text{hcp-Zr}]} - 12(1-y-z) \frac{U_{\text{tot}}[\text{bcc-Fe}]}{N_{\text{atom}}[\text{bcc-Fe}]} - 12y \frac{U_{\text{tot}}[\text{hcp-Co}]}{N_{\text{atom}}[\text{hcp-Co}]} - 12z \frac{U_{\text{tot}}[\text{hcp-Ti}]}{N_{\text{atom}}[\text{hcp-Ti}]}.
\]

(S1)

### TABLE S1. Calculated energy for the reference elemental systems based on the local basis sets as described in the text. The data for bcc-Fe, hcp-Co, and α-Sm are taken from Ref. [S9] and reproduced here for the convenience of reference.

| System | N$_{\text{atom}}$[M] | $U_{\text{tot}}$ [eV] |
|--------|-------------------|------------------|
| hcp-Ti | 2                 | -3227.8          |
| hcp-Zr | 2                 | -2634.5          |
| bcc-Fe | 1                 | -2437.4          |
| hcp-Co | 2                 | -5830.3          |
| α-Sm  | 9                 | -11383           |

### Supplemental Material for “Doped SmFe$_{12}$ for permanent-magnet utility: ab initio material design integrated with experimental characterization”

We describe the details of our computational setup used in the present work combining ab initio electronic structure calculations and experimental data from magnetic neutron scattering.

### AB INITIO STRUCTURE OPTIMIZATION OF STOICHIOMETRIC COMPOUNDS AND COMPOUNDS ON DISCRETE POINTS IN CHEMICAL COMPOSITION SPACE

The structure optimization has been done utilizing the open-source package for ab initio electronic structure calculations, OpenMX [S11–S6] which works on the basis of pseudopotentials [S7, S8] and localized basis sets. Present type of ab initio structure optimization utilizing OpenMX to evaluate the formation energy referring to elemental systems have been described elsewhere [S9]. We concisely describe what is extensively used in the present study. The choice of the local basis set has been the followings: Sm8.0$_{\text{0C}}$-s2p2d2f1, Fe6.0$_{\text{s2p2d1}}$, Co6.0$_{\text{s2p2d2f1}}$, Ti7.0$_{\text{f1}}$-s3p3d3f1, and Zr7.0$_{\text{f1}}$-s3p3d3f1, within the generalized gradient approximation (GGA) according to Perdew, Burke, and Enzerhof (PBE) [S10]. Partial core correction in the open-core approximation for Sm is set both for $\alpha$-Sm as the reference system and the target compound SmFe$_{12}$. Convergence with respect to the number of k-points and the cutoff energy is monitored. Given a material M, the optimized structure comes with the calculated energy on the basis of the choice of the particular basis set as given above: we will refer to this calculated energy as “$U_{\text{tot}}[\text{M}]$” for the convenience of reference. We note that $U_{\text{tot}}$ has been defined up to the particular choice of the basis sets and the pseudopotentials specified above and it is not entirely the true total energy.
FIG. S1. (Color online) Calculated formation energy of Co-doped SmFe\textsubscript{12}, SmFe\textsubscript{11.5}Ti\textsubscript{0.5}, and SmFe\textsubscript{11}Ti. The reference systems are the ingredient elements.

FIG. S2. (Color online) Calculated formation energy of M-doped SmFe\textsubscript{12} (M=Ti, Co, and Zr). The reference system is taken to be Sm\textsubscript{2}Fe\textsubscript{17} in the same spirit as is written in Eq. (S2). The same data as those shown in Fig. 2 in the main text are plotted with the reference systems set to be Sm\textsubscript{2}Fe\textsubscript{17}.

Here $N_{\text{atom}}[\alpha\text{-Sm}] = 9$, $N_{\text{atom}}[\text{hcp-Zr}] = 2$, $N_{\text{atom}}[\text{bcc-Fe}] = 1$, $N_{\text{atom}}[\text{hcp-Co}] = 2$, and $N_{\text{atom}}[\text{hcp-Ti}] = 2$, are the number atoms in the unit cell of the elemental systems. Calculated results for the formation energy of Co-doped SmFe\textsubscript{12}, SmFe\textsubscript{11.5}Ti\textsubscript{0.5}, and SmFe\textsubscript{11}Ti with respect to the concentration of Co are shown in Fig. S1. Referring to Fig. 2 in the main text and results of previous works, we have selectively put Ti in the Fe(8i) sublattice and Co in the Fe(8f) sublattice in order to get the overall trend of the formation energy with respect to the concentration of doped Co. It is again confirmed that SmFe\textsubscript{12} doped with Ti significantly gains the formation energy. Also the presence of Co helps the formation energy to be negative and large: Co doping in SmFe\textsubscript{12} can be the rare case where both of the strong ferromagnetism and structure stability can be gained at the same time, as long as possible other compounds with different crystal structure do not compete severely in the formation.

In the present case of the assessment of formation of SmFe\textsubscript{12}, the most probable competing phase would be Sm\textsubscript{2}Fe\textsubscript{17}. The crystal structure of Sm\textsubscript{2}Fe\textsubscript{17} is common among 4f-3d intermetallic compounds in REPM’s, such as Sm\textsubscript{2}Co\textsubscript{17} in the main cell phase of the Sm-Co magnet that was the champion magnet in 1970’s and Sm\textsubscript{2}Fe\textsubscript{17}N\textsubscript{x} that has been a candidate since early 1990’s to potentially go beyond Nd\textsubscript{2}Fe\textsubscript{14}B-based REPM. A relative formation energy of SmT\textsubscript{12} referring to Sm\textsubscript{2}T\textsubscript{17} (T=Fe or Co), $\Delta E_{\text{form}}^\text{relative}$, can be defined as follows,

$$
\Delta E_{\text{form}}^\text{relative}[\text{SmFe12}] = \frac{U_{\text{tot}}[\text{SmFe12}]}{N_{\text{fu}}[\text{SmFe12}]} - \frac{U_{\text{tot}}[\text{SmFe17}]}{2 N_{\text{fu}}[\text{SmFe17}]} - \frac{7 U_{\text{tot}}[\text{bcc-Fe}]}{2 N_{\text{atom}}[\text{bcc-Fe}]} \quad (S2)
$$
TABLE S2. Calculated energy with the optimized structure for the target compounds SmFe$_{12}$ and SmCo$_{12}$ and the corresponding data for the reference systems Sm$_2$Fe$_{17}$ and Sm$_2$Co$_{17}$, respectively. Number of formula units in the optimized structure is denoted as $N_{fu}$.

|       | $U_{tot}$ [eV] | $N_{fu}$ |
|-------|---------------|----------|
| SmFe$_{12}$ | -61026        | 2        |
| SmCo$_{12}$ | -72494        | 2        |
| Sm$_2$Fe$_{17}$ | -43965        | 1        |
| Sm$_2$Co$_{17}$ | -52089        | 1        |

AB INITIO INTERPOLATION FOR ALLOYS

Fractional parameters of the chemical composition can be continuously explored with coherent potential approximation (CPA) for random alloys. Korringa-Kohn-Rostoker (KKR) [13] Green’s function method combined with CPA (KKR-CPA) provides a convenient way to obtain an interpolated electronic structure, e.g. for Sm(Fe$_{1-y}$Co$_y$)$_{12}$ with $0 < y < 1$, between the stoichiometric limits of SmFe$_{12}$ and SmCo$_{12}$. We have used the implementation of KKR-CPA in AkaiKKR [14].

KKR-CPA can yield a reliable estimate of magnetization and magnetic exchange couplings for magnetic alloys as a continuous function of the composition parameters. Unfortunately, the absolute value of calculated energy, which we denote here by $E_{tot}^{KKRCPA}$, suffer from a systematic deviation due to a cutoff parameter $l_{max}$ in the expansion...
with respect to spherical harmonics in solving the multiple scattering problem at the core of KKR Green’s function method. In the present calculations we set $l_{\text{max}} = 2$ for all elements which should be well justified within the open-core approximation assuming well localized 4$f$-electrons. Comparison of calculated energy between different materials can be tricky within KKR-CPA but it is feasible to observe the trend in the calculated energy as long as the range of the target materials is restricted within the same type of crystal structure. Thus mixing energy $\Delta E_{\text{mix}}$ of an alloy defined in Eq. (S4) below can be combined with the formation energy calculated for the stoichiometric compounds to assess an interpolated formation energy for alloys.

$$\Delta E_{\text{mix}}[\text{Sm}(\text{Fe}_{1-x} \text{Co}_x)_{12}] \equiv E_{\text{tot}}^{\text{KKR-CPA}}[\text{Sm}(\text{Fe}_{1-x} \text{Co}_x)_{12}] - (1 - x)E_{\text{tot}}^{\text{KKR-CPA}}[\text{SmFe}_{12}] - xE_{\text{tot}}^{\text{KKR-CPA}}[\text{SmCo}_{12}] \quad (S4)$$

Combining the formation energy for the stoichiometric compounds and the mixing energy for alloys, an interpolated formation energy for the alloy can be estimated as follows:

$$\Delta E_{\text{form}}^{\text{relative}}[\text{Sm}(\text{Fe}_{1-y} \text{Co}_y)_{12}] \simeq (1 - x)\Delta E_{\text{form}}^{\text{relative}}[\text{SmFe}_{12}] + \Delta E_{\text{mix}}[\text{Sm}(\text{Fe}_{1-x} \text{Co}_x)_{12}] + x\Delta E_{\text{form}}^{\text{relative}}[\text{SmCo}_{12}] \quad (S5)$$

The results for Sm(Fe$_{1-y}$Co$_y$)$_{12}$ are shown in Fig. S3. It is seen that 40% of Co can bring the formation energy of the 1:12 phase almost on a par with the formation energy of 2:17 phase.

FIG. S4. (Color online) The scheme of the “LDA+Rietveld” self-consistent iterations.

SELF-CONSISTENT ITERATIONS BETWEEN AB INITIO KKR-CPA AND RIETVELD ANALYSIS OF MAGNETIC NEUTRON SCATTERING DATA (“LDA+RIETVELD”)

Rietveld refinement of the neutron scattering data for Sm$_{0.8}$Zr$_{0.2}$(Fe$_{0.7}$Co$_{0.3}$)$_{11.25}$Ti$_{0.75}$ has been done utilizing the FullProf program [S15]. AkaiKKR [S14] was employed to calculate the magnetic moments of each atom from first principles with the lattice structure information provided by Rietveld analysis as the input. Then the output of AkaiKKR for calculated magnetic moments is fed back to the Rietveld analysis in the next stage, and the overall process is iterated until the parameters in the inputs and the outputs converge. The scheme for this type of self-consistent iteration is shown in Fig. S4 and the initial shot of the Rietveld analysis is shown in Fig. S5.

It is to be noted that the experimental measurements are done at room temperature and ab initio calculations are done at zero temperature. Since our Co-containing samples come with sufficiently high Curie temperatures beyond 800K [S17], we regard that room temperature is close enough to zero temperature for the present analysis. If the Curie temperature of the sample is not quite high, we would turn to ab initio finite temperature calculations formulated on the basis of KKR-CPA [S18–S24] at the cost of some extra computational time. For Co-doped SmFe$_{12}$, we can safely skip this.

Remarkably, the convergence of the overall LDA+Rietveld iteration is achieved within only a few iteration steps as are shown in Table S5 with the input and output parameters of KKR-CPA. Here we count a set of Rietveld
FIG. S5. (Color online) The initial shot of the Rietveld analysis of which output makes an input to ab initio KKR-CPA in the overall “LDA+Rietveld” iteration.

analysis and ab initio calculation as one iteration step. We observe that either Sm(2a) or Fe(8i) can accommodate the doped Zr atoms in an equally plausible way. Thus the message from the data from the ab initio structure optimization for the site preference of Zr is confirmed in the analysis of the neutron scattering data for the real sample, Sm$_{0.8}$Zr$_{0.2}$(Fe$_{0.75}$Co$_{0.25}$)$_{11.25}$Ti$_{0.75}$. Details of the Rietveld analysis together with a wider range of target compounds will be reported elsewhere [S25].

EXTRACTING AN OPTIMAL SET OF THE CHEMICAL COMPOSITION PARAMETERS

On a fixed lattice of SmFe$_{12}$ [S16], we inspect the derivative of the target observables as a function of the chemical composition parameters, namely, $x$, $y$, $z$, and $z'$ in (Sm$_{1-x}$Zr$_x$)(Fe$_{1-y-z-z'}$Co$_y$Ti$_z$Zr$_{z'}$)$_{12}$. Fixed-lattice approximation has been employed here on the assumption that chemical composition i.e. the variation in the electron number affects the intrinsic properties more significantly than the variation in the lattice parameters does as long as the linear extrapolation around a reasonable stoichiometric limit [S16] is attempted. Also the effect of the celebrated Slater-Pauling curve can be more easily demonstrated with the smaller lattice constants. Thus the smaller ab initio parameter set from Table I in the main text has been taken. The other parameter sets would yield the similar messages. The overall data can be glanced in Fig. S6. Here the point is to confirm the existence of the linear regime spanning a reasonable range around the pristine/stoichiometric limit in the chemical composition space. Then within such linear regime, we can discuss at which parameter range the target observables can be optimized on demand.

From the data shown in Fig. S6, the derivative of an observable $O$ around the pristine limit is obtained as a difference between $c = 0$ and $c = 0.01$, where $c = x$, $y$, $z$, or $z'$ is the concentration of the dopant elements, and then multiplied by 100:

$$\frac{\partial O}{\partial c} \equiv \frac{O|_{c=0.01} - O|_{c=0}}{0.01} \quad (S6)$$

Numbers during such derivation of the derivative matrix in the main text are displayed in Table S4.

ELECTRON DOPING PICTURE FOR (SM,ZR)FE$_{12}$

Co-doped SmFe$_{12}$ on a fixed lattice of computational optimization [S16] nicely shows the Slater-Pauling curve as shown in Fig. S6 (b). The origin of this can be tracked down to the residual density of states around the Fermi level in the majority spin band as shown in Fig. S7 (a). This contribution comes mostly from the Fe(8f) sublattice. With the introduction of Co, extra electrons are added in the minority spin band, and we have noted that the analogous effect is given by Zr and also by Ce doped into the Sm(2a) sublattice. As a comparison calculated density of states for
FIG. S6. Deriving the derivative matrix of the intrinsic properties for (Sm$_{1-x}$Zr$_{x}$)(Fe$_{1-y}$Co$_y$Ti$_z$)$_{12}$ around the pristine limit, SmFe$_{12}$, from the calculated data via KKR-CPA using AkaikKKR. Dependence of magnetization $M$, Curie temperature $T_{Curie}$, and Sm-Fe indirect exchange couplings $J_{RT}$ for Fe(8i), Fe(8j), Fe(8f) that are crucial for anisotropy field in the operation temperature range, are plotted with respect to the concentration of dopant elements, Zr, Co, and Ti. For Zr two possible doped sublattices, Sm(2a) and Fe(8i), are explored.
(a) Zr in Sm(2a)

| KKR-CPA | step 1 | step 2 | step 3 |
|---------|--------|--------|--------|
|         | inputs | outputs [\(\mu_B\)] | inputs | outputs [\(\mu_B\)] | inputs | outputs [\(\mu_B\)] |
| 8f Fe   | 69.2\% | 1.89946 | 70.4\% | 1.89762 | 70.4\% | 1.89768 |
| Co      | 30.8\% | 1.32717 | 29.6\% | 1.32660 | 29.6\% | 1.32665 |
| 8i Fe   | \(x_i = 0.35617\), 73.6\% | 2.50941 | \(x_i = 0.35619\), 72.4\% | 2.50494 | \(x_i = 0.3562\), 72.4\% | 2.50471 |
| Co      | 8\%    | 1.66443 | 8.8\%  | 1.66101 | 8.8\%  | 1.66083 |
| Ti      | 18.8\% | -0.75328 | 18.8\% | -0.75300 | 18.8\% | -0.75306 |
| 8j Fe   | \(x_j = 0.27678\), 68\%  | 2.28426 | \(x_j = 0.27645\), 68\%  | 2.28343 | \(x_j = 0.27644\), 68\%  | 2.28351 |
| Co      | 32\%   | 1.47931 | 32\%   | 1.47928 | 32\%   | 1.47936 |
| 2a Sm   | 80\%   | -0.41385 | 80\%   | -0.41207 | 80\%   | -0.41197 |
| Zr      | 20\%   | -0.41066 | 20\%   | -0.41000 | 20\%   | -0.40995 |

for the unit cell

(b) Zr in Fe(8i)

| KKR-CPA | step 1 | step 2 | step 3 |
|---------|--------|--------|--------|
|         | inputs | outputs [\(\mu_B\)] | inputs | outputs [\(\mu_B\)] | inputs | outputs [\(\mu_B\)] |
| 8f Fe   | 69.17\% | 1.82528 | 70.63\% | 1.82613 | 70.63\% | 1.82611 |
| Co      | 30.83\% | 1.26294 | 29.37\% | 1.26432 | 29.37\% | 1.26431 |
| 8i Fe   | \(x_i = 0.35515\), 70\%  | 2.32271 | \(x_i = 0.35532\), 68.77\% | 2.51612 | \(x_i = 0.35532\), 68.77\% | 2.51594 |
| Co      | 6.32\%  | 1.66443 | 7.51\%  | 1.66825 | 7.51\%  | 1.66809 |
| Ti      | 18.57\% | -0.71585 | 18.57\% | -0.71660 | 18.57\% | -0.71663 |
| Zr      | 5.13\%  | -0.43444 | 5.13\%  | -0.43445 | 5.13\%  | -0.43446 |
| 8j Fe   | \(x_j = 0.27717\), 68.379\% | 2.23359 | \(x_j = 0.27685\), 68.25\% | 2.23380 | \(x_j = 0.27683\), 68.25\% | 2.23387 |
| Co      | 31.62\% | 1.42782 | 31.75\% | 1.42873 | 31.75\% | 1.42880 |
| 2a Sm   | 100\%  | -0.40525 | 100\%  | -0.40270 | 100\%  | -0.40259 |

for the unit cell

TABLE S3. Proceedings of the “LDA+Rietveld” iteration. (a) assuming that Zr resides in Sm(2a) and (b) Zr resides only in Fe(8i). We find that either assumption works on a par as long as the Rietveld analysis combined with ab initio KKR-CPA is concerned.

ZrFe\(_{12}\) and CeFe\(_{12}\) are shown in Figs. S7 (b), (c), and (d) for the data projected onto the Fe(8f) atoms, Fe(8i), and Fe(8j), respectively. In Fig. S7 (b) it is seen that replacement of Sm with Zr or Ce has pushed down the majority-spin band down below the Fermi level, leading to the enhancement of magnetization.

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Table S4. Numbers for the calculated derivatives from finite difference between the pristine limit and 1% doped systems for Sm$_{1-x}$Zr$_x$(Fe$_{1-y-z}$Co$_y$Ti$_z$)$_{12}$.  

(a) Raw data

| pristine | $x = 0.01$ | $y = 0.01$ | $z = 0.01$ | $z' = 0.01$ |
|----------|------------|------------|------------|-------------|
| $M$ [$\mu_B$/formula unit] | 24.1568 | 24.1627 | 24.2445 | 23.9738 | 23.9853 |
| $T_{Curie}$ [K] | 825.377 | 827.001 | 848.566 | 825.219 | 823.075 |
| $J_{RT}(5f)$ [meV] | 2.799074 | 2.801749 | 2.827002 | 2.793691 | 2.788072 |
| $J_{RT}(8i)$ [meV] | 3.986962 | 3.991619 | 4.025465 | 3.999788 | 3.992307 |
| $J_{RT}(8j)$ [meV] | 3.39035 | 3.394893 | 3.415285 | 3.385382 | 3.383555 |

(b) The derivatives defined as Eq. S6

| $\partial M/\partial c$ [$\mu_B$/formula unit] | $x$ | $y$ | $z$ | $z'$ |
|----------------------------------------------|-----|-----|-----|-----|
| 0.59 | 8.77 | -18.3 | -17.15 |
| $\partial T_{Curie}/\partial c$ [K] | 162.4 | 2318.9 | -15.8 | -230.2 |
| $\partial J_{RT}(8f)/\partial c$ [meV] | 0.2675 | 2.7928 | -0.5383 | -1.0372 |
| $\partial J_{RT}(8i)/\partial c$ [meV] | 0.4657 | 3.8503 | 1.2826 | 0.5345 |
| $\partial J_{RT}(8j)/\partial c$ [meV] | 0.4588 | 2.498 | -0.4923 | -0.675 |

(c) Normalized derivatives, as used in the main text

| $(\partial M/\partial c)/M$ | $x$ | $y$ | $z$ | $z'$ |
|--------------------------|-----|-----|-----|-----|
| 0.0244238 | 0.363045 | -0.757551 | -0.709945 |
| $(\partial T_{Curie}/\partial c)/T_{Curie}$ | 0.196759 | 2.8095 | -0.0191428 | -0.278903 |
| $(\partial J_{RT}(8f)/\partial c)/J_{RT}(8f)$ | 0.0955673 | 0.997759 | -0.192314 | -0.370551 |
| $(\partial J_{RT}(8i)/\partial c)/J_{RT}(8i)$ | 0.116806 | 0.965273 | 0.321699 | 0.134062 |
| $(\partial J_{RT}(8j)/\partial c)/J_{RT}(8j)$ | 0.135327 | 0.736807 | -0.145208 | -0.199097 |

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FIG. S7. (Color online) (a) Calculated density of states projected onto Fe atoms for the pristine SmFe$_{12}$ on an optimized lattice \cite{S16}. The arrow in the plot points to the extra density of states in the majority spin state projected onto Fe(8\textit{f}). Additional Co reduces this region leading to the Slater-Pauling curve. (b) Calculated density of states projected onto Fe(8\textit{f}) atoms for SmFe$_{12}$, ZrFe$_{12}$, and CeFe$_{12}$ on the same fixed lattice. The full-line arrow in the plot points to the majority-spin density of states on the Fermi level which is seen significantly mostly for SmFe$_{12}$. Dotted arrow points to the relatively sparse contribution from the majority spin of Fe(8\textit{f}) in CeFe$_{12}$ and ZrFe$_{12}$, which means that magnetic moments on Fe(8\textit{f}) are close to saturation for those materials. (c) and (d): Analogous data to (b) for Fe(8\textit{i}) and Fe(8\textit{j}), respectively.