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Potential High-Performance Magnet Materials: Co- and Al-alloyed Sm₂Fe₁₇

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(Dated: April 6, 2022)

Abstract

Sm₂Fe₁₇ has long been known as a potential high-performance magnet whose deficiencies - planar anisotropy and lower-than-optimal T_c - can be remedied by Nitrogen addition, but which presents synthesis difficulties. Herein we apply first-principles calculations to search for alternative low-cost, high-performance permanent magnets in this family, by exploring simultaneous Fe and Al substitution. Specifically, the goal is to improve properties of Sm₂Fe₁₄Al₃, easy-plane magnet at stoichiometric composition. Density functional theory calculations were executed for three series of compounds, i.e., Sm₂(Fe_{1-x}Co_x)₁₄Al₃, Sm₂(Fe_{1-x}Co_x)₁₅Al₂ and Sm₂(Fe_{1-x}Co_x)₁₆Al. We find that substitution of Fe with 12-18 of Co in % Sm₂Fe₁₄Al₃ modifies the magnetic anisotropy type from easy plane to easy axis with a substantial anisotropy of 7.1 MJ/m³. We also demonstrate that the largest part of magnetic anisotropy is introduced by 4f Sm atom electrons. Thus, the rotation of magnetic moment orientation from $\langle 1\bar{10} \rangle$ to $\langle 111 \rangle$ is followed by an increase of occupied 4f-states number and, as a result, the orbital part of the magnetic moment of one of the Sm atoms. This increase of the occupied 4f-states number at an energy \sim -4.3 eV results in a significant reduction of band structure energy. The substitution of Fe by Co does not significantly reduce the magnetization of the compound and keeps it slightly above 1 T. This combination of magnetic anisotropy and magnetization makes the compound a promising candidate for permanent magnet.

Keywords: permanent magnets, magnetic anisotropy, first-principles calculation, samarium compounds

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I. INTRODUCTION

Three decades ago, Coey et al [1] discovered that nitrogenation of Sm_2Fe_{17} , thus forming $Sm_2Fe_{17}N_3$, remedied the two main deficiencies preventing its usage as a permanent magnet material: its relatively low Curie point of 390 K, and its planar anisotropy. Indeed, the fully nitrogenated sample shows a Curie point exceeding 700 K and a unaxial anisotropy much higher than the 4.5 MJ/m³ room-temperature value for the permanent magnet material Nd₂Fe₁₄B.

Despite this exceptional result, $Sm_2Fe_{17}N_3$ is today relegated to usage as a bonded magnet material with energy products of only 13 MG-Oe [2], far below the ~ 50 MG-Oe that could be expected for sintered magnets based on its intrinsic properties. The reason for this is its hightemperature decomposition which has to date precluded its sintering (although it remains a subject of active research within the U.S. Critical Materials Institute and elsewhere).

In this theoretical work we explore whether it is possible to remedy the difficulties of Sm_2Fe_{17} in another manner, specifically by co-alloying with Cobalt and Aluminum. The use of Cobalt is a time-honored strategy for increasing the Curie point of Iron-based ferromagnetic materials, with this effect present here, but there is additional evidence [3] showing that, surprisingly, Aluminum alloying shows much the same effect in Sm_2Fe_{17} [4, 5] (see also results of Fe substitution by iso-electronic to Al, Ga in the publication by Shen *et.al.* [6]). The question then becomes whether the simultaneous combination of Aluminum and Cobalt succeeds in establishing the substantial uniaxial anisotropy that is a hallmark of good permanent magnet materials. Note that Sm_2Co_{17} , at the Cobalt-rich end of the phase diagram, exhibits significant uniaxial anisotropy [7] (usually enhanced by Zr substitution [8]), but that an inability to maintain this uniaxial behavior for increasing amounts of Iron substitution presently limits maximum performance to 34 MG-Oe ([9]). This is substantially below the 55 MG-Oe presently achieved for Nd₂Fe₁₄B. This lower performance also comes at a large, undesirable cost due to the substantial usage (as much as 65 weight percent) of the costly Cobalt.

Here we present theoretical results suggesting that low-cost, high-performance permanent magnets with energy products in the 25-30 MG-Oe range, well within the range of existing SmCo magnets, may be made within this family, at far lower Cobalt concentrations - approximately 10 to 13 weight percent - than presently employed in SmCo magnets. These results are based on state-of-the-art, all electron calculations within the GGA+U approximation with the Iron/Cobalt disorder treated using the virtual crystal approximation. The remainder of this paper is organized as follows. In the next section we present our Theoretical Methods, followed by the Results, a Discussion section, and a Conclusion.

II. THEORETICAL METHODS

The Sm_2Fe_{17} based materials with certain of the Fe atoms substituted by Co or Al are ordered within the Th_2Zn_17 type crystal structure with the R3m space group [4]. Its crystal structure is shown in Fig. 1, where Fe atoms are shown by small bronze color spheres, the largest spheres of purple color corresponds to Sm atoms, while midsize blue spheres are Al. Due to spin-orbit coupling the symmetry of the crystal is reduced and the structure is defined by nine nonequivalent groups of Fe atom, two different Sm atoms and two groups of Al atoms enumerated by corresponding symbols on each sphere in the figure.



FIG. 1: Three different orientations of Sm₂Fe₁₄Al₃ crystal structure, (a) general orientation, (b) projection along A and (c) along C axis, respectively. Fe atoms are shown smallest copper color spheres, Sm - largest purple spheres and the Al atoms are shown of blue color. The figure was obtained using VESTA graphical package [10].

First-principles calculations were performed within the density functional theory [11] (DFT) approximation using the linearized augmented plane-wave (LAPW) method [12–14] as implemented within the WIEN2K code [15]. The LAPW "muffin-tin" spheres of radii 2.5 Bohr , 2.19 Bohr and 2.14 Bohr for Sm, Fe and Al, respectively, together with $RK_{max} = 8.0$ are used. For the electronic structure calculations the experimental lattice parameters are used, while atomic

positions are relaxed until the forces on all the atoms are less than 1 mRy/Bohr. In the calculations the exchange-correlation energy was calculated using generalized gradient approximation (GGA) with the parametrization by Perdew, Burke, and Ernzerhof [16] (PBE). The Brillouin zone (BZ) summations were carried out over a 1000 k-points in full BZ and the MAE convergence for some specific Co concentrations was checked by summation over up to 4000 k-points. To calculate the MAE spin-orbit coupling (SOC) is included using a second-variation approach [17]. The fully self-consistency calculations were executed for different magnetic moments orientation. It's important since Sm 4f-electrons SOC are non-perturbative. A regular DFT approach is failing to reproduce localized character of correlated 4f-electrons in rare earth metals. Thus, the 4f-electron correlations are incorporated within the DFT+U approximation [18] using the selfinteraction correction scheme [19–21], which only depends on $U_{eff} = U - J$, taken here as 5 eV for the Sm 4f – electrons. While the *d*-electrons in this type of materials are described accurately enough within a regular DFT approach [22]. It's worth mentioning that U and J values do not have rigorous definition. Here this choice is close to values, $U_f \approx 5.2$ eV and $J_f \approx 0.75$ eV, obtained through the derivatives of the atomic levels with respect to their occupancies [23] as it was obtained in publication by Larson et al [24] discussing magnetic anisotropy in SmCo₅ compound. Also, it's supported by detailed comparison of theoretical results for magnetic moments with experiment in Sm-Fe compounds [22].

The magnetic anisotropy energy (MAE) in this system is calculated as a difference between the total energies of the system with the orientation of the magnetic moments along the rhombohedral $\langle 1\bar{1}0 \rangle$ (planar) and $\langle 111 \rangle$ (uniaxial) directions, MAE = $E(\langle 1\bar{1}0 \rangle) - E(\langle 111 \rangle)$. Thus, positive MAE corresponds to easy axis anisotropy. The alloying of Fe with Co is modeled using the virtual crystal approximation [25] (VCA). A similar approach has been used to investigate the result of Co substitution by Fe in Ce₂Co₁₇ [26].

It is well known that the VCA is generally applicable for an alloy of components satisfying the condition $\Delta \ll W$, where Δ is difference between the bands center and W is bands center. This condition is met in alloys of periodic table neighboring elements such as Fe, Co and Ni (see for example the discussion in publications [27–29]). Another way to model the alloying effect is to use a super-cell approximation. However, this approach generally destroys the original symmetry of the crystal and results in significant MAE calculation accuracy reduction; it is particularly impractical where co-alloying, as studied here, is investigated. Herein, the substitution of Al to pseudo-binary Fe_{1-x}Co_x is also investigated. Since, the difference between Fe and Al band

centers is comparable with Fe *d*-band width the VCA is not applicable. To overcome this problem all equivalent Al atoms (from three Al atom positions two are equivalent) are substituted by Fe. Thus, in the current investigation the MAE is calculated in three systems $Sm_2(Fe_{1-x}Co_x)_{14}Al_3$, $Sm_2(Fe_{1-x}Co_x)_{15}Al_2$ and $Sm_2(Fe_{1-x}Co_x)_{16}Al$.

III. RESULTS

The atom resolved orbital and spin moment results are summarized in the Tables I for $Sm_2(Fe_{1-x}Co_x)_{14}Al_3$ with two Co atoms concentrations, x = 0 and x = 15 %, respectively. Sm atoms orbital and spin magnetic moments obey the general trend for rare-earth metals which declares that, roughly speaking, the spin part of magnetic moment is antiparallel to the orbital one in first half of the RE series and parallel in the second half [30]. The spin part of Sm atoms magnetic moment is oriented in the direction opposite to Fe/Co moments and equal to $\sim 5.3 \ \mu_B$. Such an ordering corresponds to lower energy (see for example discussion in publication [31]). This Sm atom's negative contribution reduces the total magnetic moment of the system. However, it is partially compensated by a $\sim 2 \mu_B$ positive Sm orbital moment and resulting magnetic moment at most promising composition, Co concentration x = 15%, equals 23.4 μ_B per cell or 1.01 T. This makes this compound promising permanent magnet, as it implies potential energy products in the 25 MG-Oe range. From the result presented in Tab. I it can be seen that Fe/Co orbital moments, 0.05-0.08 μ_B , are much smaller than those for Sm. This is not surprising taking in consideration the usual quenching of 3d orbital moments. Consequently, the largest part of the magnetic anisotropy is contributed by the Sm atoms. The size of the Sm atom orbital moment depends on the moment direction and changes with Co atom concentration (Tab. I). Thus, at stoichiometry the two Sm atoms orbital moments 1.98 and 2.16 μ_B in $\langle 1\bar{1}0 \rangle$ direction (easy plane) are reduced to 1.97 and 1.98 μ_B in (111) direction (easy axis). While, at x = 15% the trend is opposite and 1.53 and 2.02 μ_B orbital moments increase to values 2.19 and 2.17 μ_B with moments direction change from $\langle 110 \rangle$ to $\langle 111 \rangle$, respectively. This trend correlates with the MAE sign change from negative at x = 0 to positive at x = 15% (Fig. 2) and reflects the general tendency to increase orbital moment along the direction corresponding to the lowest energy. The finding is in agreement with Bruno's theorem [32] postulating that the MAE is directly proportional to the anisotropy of the orbital magnetic moment.

The full calculated MAE dependence on Co concentration, x, is presented in Fig. 2c. As can be

	Fe ₁	Fe ₂	Fe ₃	Fe ₄	Fe ₅	Fe ₆	Fe ₇	Fe ₈	Fe ₉	Sm ₁	Sm ₂	Al ₁	Al_2	interstitial
$Sm_2Fe_{14}Al_3$														
Orbital moment, $\langle 1\bar{1}0 \rangle$	0.05	0.05	0.06	0.06	0.05	0.05	0.04	0.07	0.08	1.98	2.16	0.00	0.00	
Spin moment, $\langle 1\bar{1}0 \rangle$	2.35	2.35	2.35	2.43	2.6	1.98	1.98	2.14	2.14	-5.30	-5.33	-0.10	-0.10	-1.73
Orbital moment, $\langle 111 \rangle$	0.06	0.06	0.06	0.05	0.06	0.05	0.05	0.07	0.07	1.97	1.98	0.00	0.00	
Spin moment, $\langle 111 \rangle$	2.35	2.35	2.35	2.43	2.6	1.98	1.97	2.15	2.15	-5.30	-5.36	-0.10	-0.10	-1.73
$Sm_2(Fe_{1-x}Co_x)_{14}Al_3, x = 15\%$														
Orbital moment, $\langle 1\bar{1}0 \rangle$	0.06	0.07	0.07	0.06	0.08	0.06	0.05	0.09	0.08	1.53	2.02	0.00	0.00	
Spin moment, $\langle 1\bar{1}0 \rangle$	2.26	2.26	2.27	2.33	2.53	1.96	1.96	2.06	2.06	-5.29	-5.39	-0.10	-0.10	-1.91
Orbital moment, $\langle 111 \rangle$	0.08	0.08	0.08	0.09	0.08	0.06	0.06	0.07	0.07	2.19	2.17	0.00	0.00	

 $Sm_2(Fe_{1-x}Co_x)_{14}Al_3, x = 20\%$

Spin moment, $\langle 111 \rangle$

2.28 2.28 2.28 2.35 2.53 1.98 1.98 2.09 2.08 -5.30 -5.39 -0.08 -0.08

-1.89

Orbital moment, $\langle 1\bar{1}0\rangle$	0.06	0.07	0.07	0.06	0.09	0.06	0.05	0.09	0.08	1.97	2.00	0.00	0.00	
Spin moment, $\langle 1\bar{1}0 \rangle$	2.26	2.26	2.26	2.31	2.51	1.98	1.98	2.07	2.07	-5.30	-5.36	-0.10	-0.10	-1.89
Orbital moment, $\langle 111 \rangle$	0.09	0.09	0.09	0.10	0.10	0.07	0.07	0.08	0.08	2.17	2.14	0.00	0.00	
Spin moment, $\langle 111 \rangle$	2.26	2.26	2.26	2.32	2.51	1.98	1.98	2.07	2.07	-5.32	-5.40	-0.10	-0.10	-1.90

TABLE I: Atom resolved orbital, spin and total magnetic moments in μ_B in series of compounds $Sm_2(Fe_{1-x}Co_x)_{14}Al_3$ for two orientation of magnetic moments. For notation of atoms see Fig. 1

seen, for a concentration between 12 and 18 % of Fe substitution by Co the system demonstrates easy-axis behavior, i.e. the magnetic moment is oriented along the uniaxial $\langle 111 \rangle$ direction. In the same interval of concentrations, the orbital moment oriented along the $\langle 111 \rangle$ direction is larger compared to the one along $\langle 1\bar{1}0 \rangle$. It is worth mentioning that the $\langle 111 \rangle$ Co concentration dependence is quite weak while orbital moment along $\langle 1\bar{1}0 \rangle$ dependence has a significant reduction at the concentration corresponding to positive MAE.

To find the electronic structure modification responsible for such a non-monotonic concentration dependent behavior of $\langle 1\bar{1}0 \rangle$ orbital moment we compared the electronic density of states (DOS) for two concentrations and the associated direction of magnetic moments. The partial atom resolved DOS obtained at x = 0 and magnetic moment ordered along $\langle 1\bar{1}0 \rangle$ direction is presented in Fig. 3. The Fe atoms PDOS, shown by green solid line, looks rather similar to bcc Fe DOS



FIG. 2: The concentration dependence of a) orbital magnetic moments in μ_B for orientations along $\langle 1\bar{1}0 \rangle$ and $\langle 111 \rangle$ directions shown by blue line with up triangles and green line with down triangles, respectively, b) total magnetic moment in μ_B in the system with $\langle 1\bar{1}0 \rangle$ moment orientation, and c) MAE in MJ/m³.

- almost all the majority spin states (d-states predominantly) are occupied, while all the bonding d-states in minority spin channels are occupied and anti-bonding d-states are empty. In the Fig. 3b Fermi energy, E_F , corresponds to zero energy and separates a pseudo-gap between bonding and antibonding states. In pure bcc Fe such d-state occupation is in fact responsible for ordering in the bcc structure [33, 34], due to the presence of only bonding d- occupied place Fe in the same column (Ta, Nb, V) with half filled d-states ordered in bcc structure [35]. The Al s-, p-states are shown by cyan color dots and Sm₁ and Sm₂ are shown by red dashed and blue dot-dashed lines. Sm 4f-states are placed at ~ -5 eV and ~ 4 eV (Fig. 3). From the detailed d-, f-orbital resolved Sm1 atoms PDOS in Fig. 3b one can observe that a small fraction of these d-states are located in the valence electron band at ~ -1 eV, while, mainly d-states are placed above 2 eV. Such a distribution of d-states corresponds to small negative contributions to the total magnetic moment mostly formed by 4f-states. In addition to the two main peaks, a smaller peak is formed at E_F and slightly above. This area in DOS contains approximately 1.5 electrons and is separated from the main peak at -5 eV by strong repulsion, U, to preserve the total number of electrons on Sm atoms.

To determine the main source of the anisotropy, additional calculations with spin-orbit coupling (SOC) switched off on all atoms except Sm were executed. We find that in the compound at stoichiometric composition, x = 0, the MAE changes from -7.96 MJ/m³ to -9.27 MJ/m³, i.e. the contribution of transition metals is not significant, while, at x = 15% the total MAE is reduced from 6.36 MJ/m³ to 3.85 MJ/m³. Thus even at x = 15% the largest contribution to the MAE arises from the Sm atoms. Indeed, a different orientation of magnetic moments modifies the position of Sm 4f- occupied states as is shown in Fig. 4. The connection between this DOS modification and the total energy change for two magnetic moment orientations can be found by an analysis of band structure energy,

$$E_{bnd}(E) = \sum_{\vec{k},j} e_j(\vec{k})\theta[e_j(\vec{k}) - E] = \int_{-\infty}^{E} \epsilon \cdot \text{DOS}(\epsilon)d\epsilon,$$
(1)

where $e_j(\vec{k})$ is single particle energy corresponding vector \vec{k} in the Brillouin zone and branch j, $\theta[x]$ equal to 1 for x < 0 and 0 otherwise; and DOS is the density of states. Thus for small SOC, when SOC induced electronic structure changes are smaller than compared to the crystal-field one, the E_{bnd} change gives an accurate value of the MAE. Since, according to the magnetic force theorem [36] the double counting and exchange-correlation contributions can be neglected. These contributions are in the second order of magnitude of potential change caused by the change of magnetic moment direction. Since the rare-earth metals 4f-electrons SOC is non-perturbative the analysis based on E_{bnd} is qualitative.

In Fig. 5 the difference between E_{bnd} calculated for magnetic moment along $\langle 111 \rangle$ and $\langle 1\overline{10} \rangle$ directions is presented as a function of upper limit of integration (the zero of energy is at the Fermi



FIG. 3: The Sm₂Fe₁₄Al₃ atom resolved partial DOS for the case of magnetic moment ordered along $\langle 1\bar{1}0 \rangle$ direction; a) d-, f-orbital resolved Sm1 atoms PDOS, b) all atoms. The zero energy corresponds to Fermi level.

energy). The energy difference for x = 0.0 alloy is negligibly small, but not negative as in the result obtained for total energies difference. In contrast to pure compounds, the substitution of 15 % of Co by Fe dramatically changes this dependence. At Fermi level the total energies difference is -4 eV (easy axis) and 1/3 of the total value arises from the majority spin states (shown by positive values in DOS figure), while 2/3 of it comes from the minority spin states (\downarrow). Clearly, the -4



FIG. 4: The 4f-states DOS as a function of magnetic moment direction in Sm₂(Fe_{1-x}Co_x)₁₄Al₃ for two concentrations, x, and two atoms: Sm1 a) and c) and Sm2 b) and d) inserts, respectively. The zero energy corresponds to Fermi level.

eV difference is almost fully compensated by so-called double counting contributions, i.e. the Coulomb and exchange-correlation contributions to the total energy. To emphasize our previous statement that for RE metals the band structure analysis can give only qualitative results it should be mentioned that this difference obtained from the total energy is still negative, but a few orders of magnitude smaller. Since, the $\Delta E = E_{bnd}(\langle 111 \rangle) - E_{bnd}(\langle 1\bar{1}0 \rangle)$ value is negligibly small for x = 0.0 our analysis is focused on result for alloy with x = 0.15. As was already mentioned, the main contribution ΔE is coming from minority spin states shown by the green dashed line (Fig. 5b). The MAE value oscillates between -4 and 6 eV within energy interval from -5 to -4 eV where occupied 4f-states are localized and reaches a value of \approx -2.8 eV which doesn't change until energies well above the Fermi level. In contrast to the minority states the negative value ΔE almost monotonically decreases until it reaches \approx -1.3 eV at energies -2 eV. This contribution to ΔE is defined by Fe atoms, since all majority spin states of Sm atoms are localized well above the Fermi energy.

In Fig. 6 the ΔE a) for x = 0.0 and c) for x = 0.15, respectively; and DOS for b) x = 0.0 and d) x = 0.15 respectively projected on Fe₁ atom. As was already mentioned the ΔE for x = 0.00 is almost negligible. For x = 0.15 the ΔE value at Fermi level is ≈ -0.12 eV and is collected



FIG. 5: The band structure energy difference for magnetic moments orientation along $\langle 111 \rangle$ and $\langle 1\overline{10} \rangle$ directions, ΔE , as a function of upper limit of integration calculated in $Sm_2(Fe_xCo_{1-x})_{14}Al_3$ for a) x = 0 and b) x = 0.15. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively.

from majority spin states (shown by blue dots). This behavior and resulting ΔE is similar for all nonequivalent Fe atoms. Since the total number of Fe atoms equals 14 the resulting anisotropy is close to -2 eV. Thus the spin up contribution to total ΔE shown by blue dots in Fig. 5b is defined



FIG. 6: ΔE for a) x = 0.00 and c) x = 0.15; and DOS b) x = 0.00 and d) x = 0.15, respectively, projected on Fe₁ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; $\langle 111 \rangle$ DOS is shown by red solid line, while the $\langle 1\overline{1}0 \rangle$ by blue dashed line.

by Fe atoms and, as can be seen, even if this value per atom is small multiplied by 14 Fe atoms in the cell it results in 1/3 of total MAE.

The rest of the MAE is attributed to Sm atoms. By projecting ΔE on different Sm atoms, an unexpected result was obtained. There are two nonequivalent Sm atom positions presented in Sm₂Fe₁₄Al₃ and we have obtained that the contribution of these atoms to MAE are of an opposing sign. Thus, Sm₁ contribution to ΔE is positive, $\approx 2 \text{ eV}$ and doesn't change with Fe to Co substitution, Fig. 7. The minority spin electronic states of Sm₁ atoms are formed by the 4*f*-electrons predominantly and are represented by two groups of peaks - the one occupied by ≈ 5 electrons states at -4 eV and the next one at the Fermi level and slightly above it containing the rest of the unoccupied minority spin state 4*f*-electrons. These almost empty states are moved from the occupied one by a strong interaction *U* incorporated within the GGA+U scheme. By substituting 0.15 Fe atoms by Co the additional electronic empty states are occupied and can be visualized as a "downward shift" of the states at the Fermi level in Fig. 7d. However, the contribution from these states is small since they have energy close to zero and the main contribution to the band structure energy reduction with the moment direction change is from the occupied minority spin 4*f*-states. As is evident these states are moved down to lower values of energies with change of magnetic moment direction from $\langle 111 \rangle$, shown by red solid line in Sm₂ PDOS in Fig. 7) to the $\langle 1\overline{10} \rangle$ direction, shown by red solid line, while, corresponding number of states is preserved, as well as the magnetic moment, since thew majority spin states are unoccupied. It should be mentioned



FIG. 7: ΔE for a) x = 0.00, c) x = 0.15 and e) x = 0.20; and DOS b) x = 0.00, d) x = 0.15 and f) x = 0.20, respectively, projected on Sm₂ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; the $\langle 111 \rangle$ DOS is shown by red solid line, while the $\langle 1\overline{1}0 \rangle$ by blue dashed line.

that in the spirit of the approach used in publications [37–40], for Sm atoms the ΔE is defined by the contribution $\langle L_z \rangle_{\downarrow\downarrow}$ only. This occurs since the majority spin 4f-states are almost empty at energies below the Fermi level and, also, the majority and minority spin 4f-states don't overlap. Also, as a result, the ΔE is proportional to the magnetic moment (see discussion in Supplemental to publication by Belashchenko *et.al.* [37] and references therein). By summarizing the partial atomic resolved contributions it can be seen that Fe atoms contribution to MAE is compensated by Sm₂ one and the resulting MAE is defined by Sm₁ atoms. For this atom partial ΔE and DOS are presented in Fig. 8. For x = 0.0 Sm₁ ΔE is negative, ≈ -2 eV (Fig. 8a), and is compensated by a similar in magnitude, but positive contribution from Sm₂ atoms (Fig. 7a). With an increase of the Co concentration the value of the Sm₁ contribution decreases further to negative values and



FIG. 8: ΔE for a) x = 0.00, c) x = 0.15 and e) x = 0.20; and DOS b) x = 0.00, d) x = 0.15 and f) x = 0.20, respectively, projected on Sm₁ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; the $\langle 111 \rangle$ DOS is shown by red solid line, while the $\langle 1\overline{1}0 \rangle$ by blue dashed line.

reaches -4 eV for x = 0.15 (Fig. 8c). Similarly to Sm₂, almost all ΔE modifications occur at energies from -5 to -4 eV occupied by the minority spin and the "final" value -4 eV is reached at an energy -4 eV and its modification due to the additional 0.15 Co atom electrons (small modification at Fermi level) is negligible. Visually the position of minority 4f – is slightly lower for magnetic ordering along $\langle 1\bar{1}0 \rangle$ shown by blue dashed line in corresponding PDOS (Fig. 8d). This observation contradicts with the actual result. To analyze the reason for such an inconsistency we analyze the integrated density of states (number of electrons filling the states below the energy E) together with DOS and ΔE as a function of energy, E, in the interval between -5.5 and -4 eV (Fig. 9) for x = 0.15. As was mentioned previously the 4f-states peaks for magnetic ordering along the $\langle 1\bar{1}0 \rangle$ direction shown by the blue dashed line in the negative values "y" are placed lower in energy. In full agreement with peaks localization position E_{bnd} for magnetic moment direction along $\langle 1\bar{1}0 \rangle$ is the ground state, i.e. $\Delta E > 0$, until energy passes value -4.35 eV shown by the vertical black line. At this energy the number of 4f-electrons for configuration with magnetic ordering along $\langle 111 \rangle$ shown by the red solid line in the positive area of "y" begins to be larger



FIG. 9: The a) DOS, and b) ΔE for x = 0.15, respectively, projected on Sm₁ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; the $\langle 111 \rangle$ DOS is shown by red solid line, while the $\langle 1\bar{1}0 \rangle$ by blue dashed line. The DOS in plot a) is in the area of the negative values (minority spin states), while integrated DOS is shown by lines in the positive "y" values.

than that for $\langle 1\bar{1}0 \rangle$, and it results in a negative value of ΔE . This increase in the number of states for $\langle 111 \rangle$ magnetic ordering reflects the increase of the orbital part of the magnetic moment (Tab.

I). Thus, the observed reduction mechanism of band structure energy for $\langle 111 \rangle$ magnetic ordering is consistent with Bruno's theorem. However, this rule is deviated for Co concentration x = 0.2. The orbital part of Sm atoms magnetic moment is slightly larger for $\langle 111 \rangle$ direction (Tab. I), while, MAE is negative (Fig. 2). This result could be clarified by E_{bnd} analysis. As it can be seen, the Sm₂ ΔE is not sensitive to Co concentration (Fig. 8a, c and e) and equal approximately 2 eV. It's defined by downward shift of 4f – electron states position for $\langle 1\bar{1}0 \rangle$ moments direction shown by blue dashed line in DOS (Fig. 8b, d and f). For Sm₁ atom this modification is even more pronounced. The negative ΔE value (Fig. 8a, c and e) for x = 0.0 and 0.15 is modified to slightly positive one. Again, similar to Sm₂ this modification is defined by downward shift of 4f-states (blue dashed line in Fig. 8f). It should be mentioned that this shift is similar for each Co concentration, however, for x = 0.15 it's compensated by dramatic increase Sm₁ of spin-down 4f-states for $\langle 111 \rangle$ moment orientation, Fig. 8d. The latter is reflected in change of orbital moment from 1.53 to 2.19 μ_B (Tab. I). While for Co concentration x = 0.20 the corresponding 4f-states occupation modification is not large enough to compensate downward 4f-states shift. Corresponding orbital moment changes from 1.97 to 2.17 μ_B only (Tab. I).

The calculated results for MAE for all three Sm based systems $Sm_2(Fe_{1-x}Co_x)_{14}Al_3$ (red circles), $Sm_2(Fe_{1-x}Co_x)_{15}Al_2$ (green triangles) and $Sm_2(Fe_{1-x}Co_x)_{16}Al$ are combined in one Fig. 10. To present the calculated results in some systematic way the MAE in this figure is plotted as a function of the total number of electrons in the unit cell. In each of the compounds the concentration, x, is changed from 0 to 20 %, i.e. the set of connected points corresponds to concentrations set $\{0, 5, 10, 15, 20\}$. With the *d*-band filling the MAE oscillates between negative and positive values. Similarly to the system containing three Al atoms, in $Sm_2(Fe_{1-x}Co_x)_{15}Al_2$ the calculated orbital moment and MAE obeys Bruno's theorem. Thus, for this compound both MAE is negative and the Sm atoms orbital moments along the $\langle 110 \rangle$ direction is slightly larger compared to the one oriented along the $\langle 111 \rangle$ one (2.07 vs 1.98 and 2.03 vs 1.96 μ_B for Sm₁ and Sm₂ atoms, respectively, see x = 10% result presented in Tab. II). This result looks obvious, since substitution of Al₁ atom by Fe effectively works as an addition of d-electrons to the system and it continue tendency for MAE obtained for $Sm_2(Fe_{1-x}Co_x)_{14}Al_3$ for x = 0.20, i.e. 4f-states are shifted downward for moment orientation change from $\langle 1\bar{1}0 \rangle$ to $\langle 111 \rangle$ direction, while the number of occupied 4f-states don't change significantly enough to compensate the position shift. Later is reflected in small orbital moment modification; 0.09 and 0.06 μ_B for Sm₁ and Sm₂ atoms, respectively.

For the case of $Sm_2(Fe_{1-x}Co_x)_{16}Al$ the situation is more complicate. Thus, for Sm_1 atom or-

	Fe ₁	Fe ₂	Fe ₃	Fe ₄	Fe ₅	Fe ₆	Fe ₇	Fe ₈	Fe ₉	Sm_1	Sm_2	Fe ₁₀	Al_2	interstitial
$\operatorname{Sm}_2(\operatorname{Fe}_{1-x}\operatorname{Co}_x)_{15}\operatorname{Al}_2, x = 10 \%$														
Orbital moment, $\langle 1\bar{1}0 \rangle$	0.06	0.05	0.05	0.07	0.08	0.05	0.05	0.06	0.08	2.07	2.03	0.06	0.00	
Spin moment, $\langle 1\bar{1}0 \rangle$	2.30	2.35	2.37	2.45	2.57	2.10	2.05	2.28	2.18	-5.32	-5.32	2.40	-0.10	-1.97
Orbital moment, $\langle 111 \rangle$	0.07	0.06	0.06	0.06	0.06	0.05	0.05	0.07	0.07	1.98	1.97	0.06	0.00	
Spin moment, $\langle 111 \rangle$	2.30	2.35	2.37	2.45	2.58	2.09	2.05	2.27	2.18	-5.31	-5.33	2.40	-0.10	-1.97

	Fe ₁	Fe ₂	Fe ₃	Fe ₄	Fe ₅	Fe ₆	Fe ₇	Fe ₈	Fe ₉	Sm_1	Sm_2	Al_1	Fe ₁₀	interstitial
$\operatorname{Sm}_2(\operatorname{Fe}_{1-x}\operatorname{Co}_x)_{16}\operatorname{Al}, x = 10 \%$														

Orbital moment, $\langle 1\bar{1}0\rangle$	0.07	0.06	0.06	0.07	0.07	0.04	0.04	0.07	0.04	2.03	1.54	0.00	0.07	
Spin moment, $\langle 1\bar{1}0 \rangle$	2.47	2.40	2.39	2.57	2.63	2.16	2.25	2.34	2.45	-5.32	-5.33	-0.10	2.45	-2.03
Orbital moment, $\langle 111 \rangle$	0.05	0.06	0.07	0.06	0.05	0.05	0.04	0.06	0.05	1.87	1.81	0.00	0.05	
Spin moment, $\langle 111 \rangle$	2.47	2.40	2.39	2.57	2.63	2.16	2.25	2.34	2.45	-5.32	-5.33	-0.10	2.46	-2.03

TABLE II: Atom resolved orbital, spin and total magnetic moments in μ_B in compounds Sm₂(Fe_{1-x}Co_x)₁₅Al₂ and Sm₂(Fe_{1-x}Co_x)₁₆Al for two orientation of magnetic moments. For notation of atoms see Fig. 1

bital moment reduces, while, for Sm₂ it increases. Sm₁ atom behaviour in this system is similar to Sm₂(Fe_{1-x}Co_x)₁₅Al₂ case, where is the orbital moment is slightly reduced with moment direction change from $\langle 1\bar{1}0 \rangle$ to $\langle 111 \rangle$. In combination with downward shift of 4f-states position for $\langle 1\bar{1}0 \rangle$ direction it results in positive ΔE value change. However, this band structure energy increase is compensated by Sm₂ atom energy gain, caused by significant increase of occupied 4f-states for $\langle 111 \rangle$ magnetic moment orientation, which reflects in Sm₂ orbital moment increase from 1.54 to $1.81 \mu_B$. Thus Sm₂ atom in this compound behaves similar to Sm₁ atom in Sm₂(Fe_{1-x}Co_x)₁₄Al₃, where x = 0.15. Such a switch of the main contributor to positive MAE role from Sm₁ to Sm₂ atoms could be explained from the position of 4f-states relative to Fermi energy. As it can be seen from Fig. 3b the Sm₂ 4f-states shown by blue dot-dashed line are placed higher in energy than compared to the Sm₁ one. Thus it takes larger number of electrons, which effectively results in upward shift of Fermi energy, to occupy Sm₂ atoms in a way similar to Sm₁ one.

It's worth mentioning that the easy-axis magnetic anisotropy obtained in $Sm_2(Fe_{1-x}Co_x)_{14}Al_3$,



FIG. 10: The calculated MAE in $Sm_2(Fe_{1-x}Co_x)_{14}Al_3$ (red circles), $Sm_2(Fe_{1-x}Co_x)_{15}Al_2$ (green triangles) and $Sm_2(Fe_{1-x}Co_x)_{16}Al$ (blue diamonds) systems presented as a function of total number of valence electrons

x=0.15 is preserved for wide range of U_{eff} parameters. Thus, MAE equals to 16.5, 6.4 and 3.1 MJ/m³ for U_{eff} equals 4, 5 and 6 eV, respectively.

IV. CONCLUSIONS

Recently it was demonstrated [26] that substitution of Co by Fe in Ce₂Co₁₇ results in uniaxial MAE for some concentration of Fe while preserving reasonably large magnetic moments. Here we have applied a similar approach was applied to improve the properties of Sm₂Fe₁₄Al₃, an easy-plane magnet at stoichiometric composition. First-principles calculation were performed for three series of compounds, i.e. Sm₂(Fe_{1-x}Co_x)₁₄Al₃, Sm₂(Fe_{1-x}Co_x)₁₅Al₂ and Sm₂(Fe_{1-x}Co_x)₁₆Al. We found that the Sm₂(Fe_{1-x}Co_x)₁₄Al₃ compound with Co concentration between 12 and 18 % demonstrates easy axis behavior with anisotropy as high as 7.1 MJ/m³, while Sm₂(Fe_{1-x}Co_x)₁₆Al has positive MAE for all range of Co concentration explored in current work. The largest part of MAE is introduced by Sm atoms. Thus, the change of magnetic moment direction from $\langle 1\bar{10} \rangle$ to $\langle 111 \rangle$ is followed by an increase of the occupied 4*f*-states number and, as a result, the orbital part of the magnetic moment of Sm₁ atom. This increase of occupied 4*f*-states number at energy ~ -4.3 eV results in a significant reduction of band structure energy, with the latter finding supporting

Bruno's theorem. Finally substitution of Fe by Co retains the magnetization of the original compound at slightly above 1 T. Such a large MAE in combination with magnetization value above 1 T makes the compound a promising candidate for a potential permanent magnet.

V. ACKNOWLEDGMENTS

This research was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. This research used resources of the Compute and Data Enviroment for Science (CADES) at the Oak Ridge National Lab- oratory, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC05-000R22725.

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LIST OF TABLES

- I Atom resolved orbital, spin and total magnetic moments in μ_B in series of compounds Sm₂(Fe_{1-x}Co_x)₁₄Al₃ for two orientation of magnetic moments. For notation of atoms see Fig. 1
- II Atom resolved orbital, spin and total magnetic moments in μ_B in compounds $Sm_2(Fe_{1-x}Co_x)_{15}Al_2$ and $Sm_2(Fe_{1-x}Co_x)_{16}Al$ for two orientation of magnetic moments. For notation of atoms see Fig. 1 18

7

LIST OF FIGURES

1 Three different orientations of $Sm_2Fe_{14}Al_3$ crystal structure, (a) general orientation, (b) projection along A and (c) along C axis, respectively. Fe atoms are shown smallest copper color spheres, Sm - largest purple spheres and the Al atoms are shown of blue color. The figure was obtained using VESTA graphical package [10].

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8

12

13

14

- The concentration dependence of a) orbital magnetic moments in μ_B for orientations along $\langle 1\bar{1}0 \rangle$ and $\langle 111 \rangle$ directions shown by blue line with up triangles and green line with down triangles, respectively, b) total magnetic moment in μ_B in the system with $\langle 1\bar{1}0 \rangle$ moment orientation, and c) MAE in MJ/m³.
- The Sm₂Fe₁₄Al₃ atom resolved partial DOS for the case of magnetic moment ordered along (110) direction; a) d-, f-orbital resolved Sm1 atoms PDOS, b) all
 atoms. The zero energy corresponds to Fermi level.
- 4 The 4f-states DOS as a function of magnetic moment direction in Sm₂(Fe_{1-x}Co_x)₁₄Al₃ for two concentrations, x, and two atoms: Sm1 a) and c) and Sm2 b) and d) inserts, respectively. The zero energy corresponds to Fermi level. 11
- 5 The band structure energy difference for magnetic moments orientation along $\langle 111 \rangle$ and $\langle 1\overline{1}0 \rangle$ directions, ΔE , as a function of upper limit of integration calculated in Sm₂(Fe_xCo_{1-x})₁₄Al₃ for a) x = 0 and b) x = 0.15. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively.
- ΔE for a) x = 0.00 and c) x = 0.15; and DOS b) x = 0.00 and d) x = 0.15, respectively, projected on Fe₁ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; (111) DOS is shown by red solid line, while the (110) by blue dashed line.
- 7 ΔE for a) x = 0.00, c) x = 0.15 and e) x = 0.20; and DOS b) x = 0.00, d) x = 0.15 and f) x = 0.20, respectively, projected on Sm₂ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; the $\langle 111 \rangle$ DOS is shown by red solid line, while the $\langle 1\overline{1}0 \rangle$ by blue dashed line.

- 8 ΔE for a) x = 0.00, c) x = 0.15 and e) x = 0.20; and DOS b) x = 0.00, d) x = 0.15 and f) x = 0.20, respectively, projected on Sm₁ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; the $\langle 111 \rangle$ DOS is shown by red solid line, while the $\langle 1\overline{10} \rangle$ by blue dashed line.
- 9 The a) DOS, and b) ΔE for x = 0.15, respectively, projected on Sm₁ atoms. The zero energy corresponds to Fermi level. The total value, spin down and spin up contributions are shown by solid red, dashed green and dotted blue lines, respectively; the $\langle 111 \rangle$ DOS is shown by red solid line, while the $\langle 1\overline{10} \rangle$ by blue dashed line. The DOS in plot a) is in the area of the negative values (minority spin states), while integrated DOS is shown by lines in the positive "y" values.
- 10 The calculated MAE in $\text{Sm}_2(\text{Fe}_{1-x}\text{Co}_x)_{14}\text{Al}_3$ (red circles), $\text{Sm}_2(\text{Fe}_{1-x}\text{Co}_x)_{15}\text{Al}_2$ (green triangles) and $\text{Sm}_2(\text{Fe}_{1-x}\text{Co}_x)_{16}\text{Al}$ (blue diamonds) systems presented as a function of total number of valence electrons

16

15