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Thermodynamics of $SmCo_5$ compound doped with Fe and Ni: An *ab initio* study

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ABSTRACT

$SmCo_5$ permanent magnets exhibit enormous uniaxial magnetocrystalline anisotropy energy and have a high Curie temperature. However, their low energy product is a significant deficiency. To increase the energy product in $SmCo_5$, we propose substituting cobalt with iron, that has a much larger magnetic moment, in a $SmCoNiFe_3$ magnet where nickel is used as a thermodynamic stabilizer.

1. Introduction

Three fundamental material parameters determine the intrinsic properties of hard magnetic materials: (i) spontaneous (saturation) magnetization, M_s, (ii) Curie temperature, T_c, and (iii) magnetocrystalline anisotropy energy (MAE), K_1 [1]. These three parameters all need to be large for a permanent magnet to be technologically suitable, i.e., $T_c \sim \geq 550$ K, $M_s \sim \geq 1$ MA/m, $K_1 \sim \geq 4$ MJ/m^3. The desired values of these quantities can be obtained for a magnet by combining transition-metal (TM) with rare-earth-metal (RE) atoms in various intermetallic compound [1,2].

The $SmCo_5$ (in the hexagonal $CaCu_5$-type structure) magnet exhibits an enormous uniaxial MAE of $K_1 \sim 17.2$ MJ/m^3, substantially higher than that of $Nd_2Fe_{14}B$ (Neomax) magnets ($K_1 \sim 4.9$ MJ/m^3) with almost double the Curie temperature ($T_c \sim 1020$ K) of Neomax ($T_c \sim 588$ K) [3,4]. However, $Nd_2Fe_{14}B$ currently dominates the world market for permanent magnets (~62%) [5,6], because it has the largest energy performance measured by a record energy product $(BH)_{max}$ of 512 kJ/m^3, more than twice as high as the energy product of the $SmCo_5$ magnets, $(BH)_{max}$ of 231 kJ/m^3 [3,4]. Even though $SmCo_5$ magnets are more suitable for high-temperature applications than Neomax, their world-market share is very low (~3%) due to their relatively low energy performance [5,6].

From a cost stand point, it is beneficial to substitute Co atoms with Fe because Fe in the Earth's crust is ~2000 times more abundant than Co and consequently much cheaper. In addition, Fe is a ferromagnetic metal with a very large magnetization at room temperature (1.76 MA/m [3]). However, substituting all cobalt with iron to maximize magnetization in $SmFe_5$ makes it thermodynamically unstable and it does not exist in the equilibrium Sm-Fe phase diagram. On the other hand, the alloy $Sm(Co_{1-x}Fe_x)_5$ ($CaCu_5$-type phase) has been synthesized by the melt-spinning method for $x = 0.0–0.3$ [7]. Furthermore, the Curie temperature for these $Sm(Co_{1-x}Fe_x)_5$ alloys is found to increase from ~1020 K to ~ 1080 K when increasing x from 0.0 to 0.2 [8], in contrast to the $Sm_2(Co_{1-x}Fe_x)_{17}$ alloys that show a monotonic decrease in Curie temperature with increasing Fe content [9].

The fundamental purpose of the present study is to explore the effects of adding nickel to stabilize the $Sm(Co_{1-x}Fe_x)_5$ alloys. We

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also investigate and report some interesting aspects of the magnetic properties of the $SmCo_5$ compound that were incorrectly described in some previous studies [10–13]. We employ *ab initio* calculations using four complementary techniques: (i) the scalar-relativistic projector-augmented wave (PAW) method implemented in the Vienna *ab initio* simulation package (VASP), (ii) the fully relativistic exact muffin-tin orbital method (FREMTO), (iii) the full-potential linear muffin-tin orbital method (FPLMTO), and (iv) the full-potential linearized augmented plane wave (FPLAPW) method. All methods account for all relativistic effects, the so-called spin-orbit coupling (SOC). The usage of these different methods ensures that our results are robust and independent of technical implementations, while taking advantage of the strengths of each method. Pertinent details of the computational methods are described in Ref. [14]. Results of the density-functional-theory (DFT) calculations of the ground state properties of Sm(Co-Fe-Ni)$_5$ alloys are presented in Section 2. We show results from calculations of the magnetic properties of the $SmCo_5$ compound in Section 3. Lastly, concluding remarks are presented in Section 4.

2. Ground state properties of Sm(Co-Fe-Ni)$_5$ alloys

The $SmCo_5$ compound crystallizes in the hexagonal $CaCu_5$-type structure with three non-equivalent atomic sites: Sm_1-(*1a*), Co_1-(*2c*), Co_2-(3g) (see Fig. 1) with 6 atoms per formula unit and also per computational cell.

Table 1 shows the equilibrium formula unit (f.u.) volume, bulk modulus, and the pressure derivative of the bulk modulus for the $SmCo_5$ compound computed using each of the *ab initio* methodologies. The results of the PAW calculations are shown both without ('VASP') and with ('VASP+SOC') inclusion of SOC. Similarly, the results of the EMTO calculations are shown both without ('SREMTO', 'SR' means scalar-relativistic) and with ('FREMTO') inclusion of SOC. The experimental value of the equilibrium f.u. volume is taken from Ref. [16]. Notice that the equilibrium volumes in Table 1 agree quite well with the experimental value and that including the relativistic SOC in the calculation has only a minor effect. Accounting for Coulomb correlations in the *f*-shell (FPLAPW) also has only a small influence on the equilibrium volume.

Fig. 2 shows the results of calculation of the heat of formation of $SmCo_5$ compound doped with Fe. The coherent potential approximation (CPA) implemented within the EMTO method allows a gradual substitution of Co atoms by Fe atoms on the Cu-type 3g and *2c* sites of the $CaCu_5$–type structure. We see that the EMTO-CPA calculations predict a very small region of stability ($x \leq 0.05$) for $Sm(Co_{1-x}Fe_x)_5$ alloys. The FPLMTO calculations for the $SmCo_5$ and $SmFe_5$ pseudo-binary end points give similar results to those given by the EMTO method; a simple straight-line interpolation between these points gives a region of stability of $x \leq 0.10$.

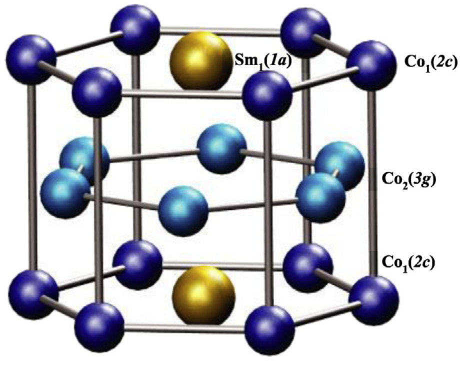

Fig. 1. Crystal structure of $SmCo_5$. The schematic is taken from Ref. [15].

Fig. 3 shows results of similar calculations for the pseudo-binary $Sm(Ni_{1-x}Fe_x)_5$ alloys. Due to the significant negative value of the heat of formation of the $SmNi_5$ compound (~−19 mRy/atom), EMTO-CPA calculations show that approximately half of the Ni atoms in $SmNi_5$ can be substituted by Fe atoms. FPLMTO calculations for the $SmNi_5$ and $SmFe_5$ end points show to an even larger extent a stabilizing effect when substituting Ni with Fe. The EMTO-CPA calculations are in excellent agreement with recent SEM/EDS measurements [17], which find that the maximum extension of $SmNi_{5-x}Fe_x$ alloys (in the $CaCu_5$-type structure) is about 50 at. % Fe, resulting in a stable formation of the $SmFe_3Ni_2$ compound.

Previous neutron-diffraction studies of $Th(Co_{1-x}Fe_x)_5$ alloys (also based on the $CaCu_5$-type structure) [18] show that the larger Fe atoms prefer to occupy the 3g-type sites, whereas the smaller Co atoms prefer to occupy the *2c*-type sites. This occupation preference has been confirmed by DFT calculations for $SmCo_5$ [19] and YCo_5 [20] compounds. According to these calculations, the total energy for Fe at the 3g site (E_{3g}) is lower that than for Fe at the *2c* site (E_{2c}) by 0.10 eV/f.u. and 0.21 eV/f.u. for $SmCo_5$ and YCo_5, respectively. Here we perform similar calculations for $SmNi_4Fe$ compound with Fe at the 3g site and Fe at the *2c* site. According to present calculations, the total energy is substantially (0.245 eV/f.u.) lower when iron sits at the 3g site. Fig. 4 shows the heat of formation within the CPA formalism of pseudo-binary $SmFe_3(Ni_{1-x}Co_x)_2$ alloys where Fe atoms occupy all 3g-type sites and the occupation of the *2c*-type sites gradually changes from pure Ni (the $SmFe_3Ni_2$ compound) to pure Co (the $SmFe_3Co_2$ compound). The present calculations show that $SmFe_3(Ni_{1-x}Co_x)_2$ alloys could remain stable until approximately half of Ni atoms are substituted by Co atoms.

3. Magnetic properties of the $SmCo_5$ compound

Table 2 presents previously reported results [10–12] of the site-projected spin, $m^{(s)}$, and orbital, $m^{(o)}$, moments of the $SmCo_5$ compound calculated by FPLAPW. The calculated total moment $m^{(tot)} = 9.90\ \mu_B/f.u.$ significantly exceeds the reported experimental values of 7.80 $\mu_B/f.u.$ [21] and 8.97 $\mu_B/f.u.$ [22]. Also, the calculated MAE, $K_1 = 40.79\ MJ/m^3$, substantially exceeds the experimental value $K_1 = 17.2\ MJ/m^3$ [3].

Although FPLAPW calculations qualitatively predict the correct axial anisotropy (positive MAE) of the $SmCo_5$ compound, we know that these results are "artificial" because of the incorrectly assumed parallel alignment between the spins of Sm and Co atoms. It is well established that spins of RE and TM atoms always align antiparallel in RE-TM compounds [23,24]. To confirm this fact, we performed total-energy (FPLAPW) calculations of the $SmCo_5$ compound as a function of the atomic volume for both parallel and antiparallel Sm and Co spin alignments. The results of these calculations (FPLAPW with $U = J = 0$), are shown in Fig. 5. The results show that the parallel spin alignment, assumed in Refs. [10–12], represents a *metastable* state, that lies a significant 7 mRy/atom above the *ground* state with antiparallel spin orientation. FPLAPW LDA+U calculations, performed with $U - J = 4.45$ eV, predicts the same conclusion (see Fig. 6): within this level of theory, the *metastable* parallel-spins state lies ~ 4 mRy/atom above the antiparallel spins *ground* state.

Tables 3–8 display the results of the site-projected spin, $m^{(s)}$, and orbital, $m^{(o)}$, moments of the $SmCo_5$ compound obtained from the different methods assuming the correct antiparallel Sm and Co spin alignment. In the case of VASP+SOC, FREMTO, and FPLMTO calculations ($U = J = 0$), as shown in Tables 3–5, respectively, the total moment is 4.18 $\mu_B/f.u.$, 4.60 $\mu_B/f.u.$, and 4.04 $\mu_B/f.u.$, respectively, which are all less than half of the reported experimental values of 7.80 $\mu_B/f.u.$ [21] or 8.97 $\mu_B/f.u.$ [22]. Accounting for Coulomb