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Electronic Structure of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ Alloys

— XPS and *ab initio* Study

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The band structure investigations for $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ alloys by means of X-ray photoelectron spectroscopy (XPS) and an *ab initio* density functional theory (DFT) calculations are presented. The aim was to determine an effect of Ni/Co substitution on the electronic structure of the alloys. Investigations have shown that the Ni/Co substitution results in a reconstruction of the valence band (VB), especially the intensity near the Fermi level decreases with Co content. An *ab initio* simulated XPS VB spectra agree qualitatively with experimental ones with the exception of the Sm-4f sub-spectra where the multiplet decomposition is observed. Calculations shown that variation of magnetization in $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ is driven mainly by the Ni/Co-3d and Sm-5d states polarization and increases linearly with rising Co content.

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1. Introduction

The rare-earth/transition-metal (RE/TM) intermetallic compounds attract currently a significant interest due to their high coercivity and a large magnetocrystalline anisotropy, driven by $3d-4f$ interactions [1]. This raises the prospect of using these intermetallics as a key component of wind-turbines, electric vehicles [2] or ultra-high density recording media [3]. Although the magnetic properties of the typical permanent magnet materials, e.g. Sm-Co and Sm-Ni, are already well recognized [4–6], there is an increasing interest in a new RE/TM compounds of high magnetic performance.

In the paper we present density functional (DFT) calculations and XPS study performed for the first time for the series of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ alloys. We focused on an effect of cobalt for nickel substitution on the electronic structure of the alloys. Our results confirmed the VB reconstruction and indicated that the Ni/Co substitution appears to be beneficial for the magnetization of the investigated alloys.

2. Experimental and computational details

The preparation of the $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ samples is described in Ref. [7]. The XPS measurements were performed with the use of a PHI 5700/660 Physical Electronics Spectrometer applying monochromatized Al K_α radiation (1486.6 eV).

Calculations were carried out using the WIEN2k code [8] based on the full-potential linearized augmented plane-wave (FP-LAPW) plus local orbital (LO) method [9]. For the core states ([Kr] for Sm and [Ne]

for Ni and Co) the fully relativistic DFT was applied while the remaining states were treated within the scalar-relativistic approximation. The spin-orbit (SO) coupling was included within the second variational approach [9] (for all atoms in SmNi_3 , SmCo_3 and for Sm atoms for fractional compositions). For the exchange-correlation potential the revised PBE generalized gradient approximation (PBEsol) [10] was applied. To account for the enhanced Coulomb correlation for Sm 4f electrons, we used the LDA+U formalism [11] with an effective Hubbard parameter $U_{eff} = 0.4$ Ry [12]. The muffin-tin radii were chosen as 1.323 Å for Sm and 1.137 Å for Ni and Co. To achieve accurate total energy convergence, the maximum value of angular momentum, the plane-wave expansion cutoff and the magnitude of the largest K -vector in the Fourier expansion was set to $L = 10$, $K_{max} = 7.0/R_{MT}$, $G_{max} = 12$, respectively. For all compositions the k -mesh with 2400 k -points in the full Brillouin zone was used. The lattice parameters were taken from the linear interpolation between our experimental data for the end point SmNi_3 , SmCo_3 compounds ($a = b = 5.0073$ Å, $c = 24.6315$ Å and $a = b = 5.0526$ Å, $c = 24.6621$ Å, respectively). The simulated XPS spectra were obtained by convolution of the partial densities of states by the Lorentzian distribution (0.25 eV) and multiplication by the corresponding cross-sections [13].

3. Results and conclusions

Our experiments have shown that $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ alloys crystallize in the PuNi_3 -type structure (space group No. 166) in which Sm atoms take single $3a$ (0, 0, 0) and double $6c$ (0, 0, z_1) positions. The Ni(Co) atoms occupy single $3b$ (0, 0, $1/2$), double $6c$ (0, 0, z_2) and sixfold $18h(x_1, -x_1, z_3)$ sites. The relaxation of atomic positions yields (x_1, z_1, z_2, z_3) parameters equal (0.4994, 0.1320, 0.3321, 0.0804) for SmNi_3 and

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(0.4993, 0.1340, 0.3326, 0.0794) for SmCo_3 (in quantitative agreement with experimental data [14]). We have investigated the site-preference (for $x = 1/9$) and magnetic structure of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ series for $x = n/9$ ($n = 0, 1, 2, 3, 6, 9$). From the total energy analysis calculated for $x = 1/9$, with single Co located at $3b$, $6c$ and $18h$ sites we found that Co atoms prefers to substitute Ni ones in $3b$ or $6c$ positions what agree with our experimental observations. Figure 1 shows the supercell with Co in $3b$ position ($x = 1/9$).

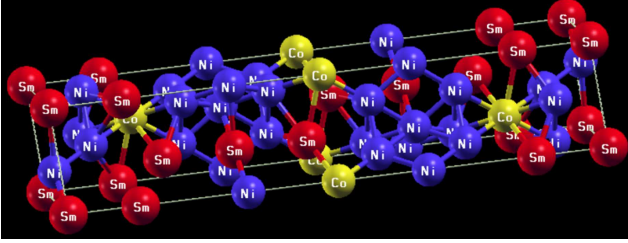


Fig. 1. The supercell used in calculations for single Co atom in $3b$ position ($x = 1/9$).

To simulate concentrations $x = 2/9$ and $3/9$ we placed the Co atoms in $6c$ and $3b + 6c$ positions. For higher concentrations the Co atoms occupy also the $18h$ positions. To test the changes of electronic structures for higher Co concentration we performed calculations, with Co occupying completely the group of $18h$ positions ($x = 6/9$).

Calculations have shown that magnetic structure of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ is sensitive to composition. Table I presents local spin and orbital magnetic moments calculated for SmNi_3 and SmCo_3 . In SmNi_3 the Sm $4f$ spin magnetic moments (μ_S^{4f}) in $3a$ and $6c$ sites polarize oppositely (AF), while for other compositions the ferromagnetic (FM) alignment of Sm μ_S^{4f} moments is energetically favorable. The exchange coupling between Sm μ_S^{4f} moments is of indirect, RKKY-type and the change of μ_S^{4f} ordering upon Co/In substitution may be ascribed to VB reconstruction and/or varying distance between $3a$ and $6c$ sites. Magnitude and ordering of Ni(Co) magnetic moments changes with composition. Polarization of μ_{3d}^{Ni} moments in SmNi_3 coincides with that of Sm in $3a$ site. In SmCo_3 magnetic moments μ_{3d}^{Co} polarize oppositely to those of Sm, whereas for fractional concentrations polarization of Ni(Co) moments coincides with that of Sm sublattice. Magnitudes of the local magnetic moments vary in the range: μ_{3d}^{Ni} (0.05–0.5 μ_B); μ_{3d}^{Co} : (1–1.5 μ_B) and μ_{5d}^{Sm} : (0.00–0.15 μ_B).

For all compositions calculations yield the Sm^{3+} configuration with $n_{4f}^{\uparrow} \approx 5$ what, with the calculated value of orbital moment ($L \approx 3$), gives $\mu_{4f}^{eff} \approx 0.58 \mu_B$ (the Hund rules give $\mu_{4f}^{eff} \approx 0.84 \mu_B$). We aware that our calculations do not reproduce second Hund correctly and give reduced values of effective moment μ_{4f}^{eff} . Recently it has been shown that magnetization of Sm sublattice in SmCo_3 can be considerably reduced ($\mu_{4f}^{eff} \approx 0.25 \mu_B$) due to mixing of the crystal field levels of the ground state

multiplet states [15]. Using $\mu_{4f}^{eff} \approx 0.58 \mu_B$ and μ_{3d}^{Ni} , μ_{3d}^{Co} , μ_{5d}^{Sm} values from Table I gives total magnetic moment equal 0.29 μ_B for SmNi_3 and 3.38 μ_B for SmCo_3 (in good agreement with available experimental data [16]). Total magnetic moment in $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ increases roughly linearly with Co contents.

TABLE I

Local spin (μ_S) and orbital (μ_L) magnetic moments in SmNi_3 and SmCo_3 compounds (in units of μ_B).

	3a (Sm)		6c (Sm)		3b	6c	18h	
	5d	4f	5d	4f	3d (Ni/Co)			
SmNi_3	μ_L	–	2.9	–	–3.1	–0.02	–0.02	–
	μ_S	–0.05	–4.98	0.11	5.01	–0.17	–0.13	–0.20
SmCo_3	μ_L	–0.01	–3.19	–0.01	–2.68	–0.04	–0.03	–
	μ_S	0.21	4.99	0.24	5.05	–1.50	–1.56	–1.37

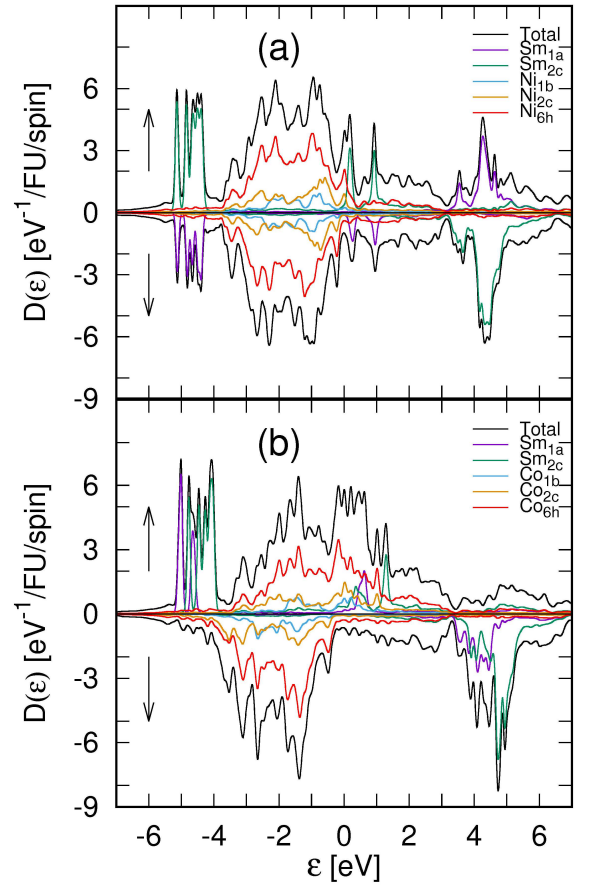


Fig. 2. Spin resolved density of states (DOS) with partial atomic contributions in SmNi_3 (part a) and SmCo_3 (part b). Vertical dot line shows the position of Fermi level.

Figure 2 presents the total DOS with a partial atomic contributions for end point SmNi_3 and SmCo_3 compounds. The VB density of states is clearly separated into the higher BE region, formed by the five Sm- $4f$ states and the lower BE region (covering the Fermi level)

formed by 3d states of Ni/Co ions occupying different positions. The remaining two empty 4f bands locate above Fermi energy. Due to different local environment of Ni atoms their 3d bands locate at different binding energies, however they form a common complex, strongly hybridized band around Fermi energy. The presence of occupied minority spin 4f band (Fig. 2a) is the consequence of the opposite spin polarization of Sm at 3a and 6c positions in SmNi_3 . The replacement of Ni by Co atoms changes the minority 3d bands only slightly while the majority TM *d*-bands undergoes essential reconstructions — it widens and shifts above Fermi energy.

Figure 3 compares the simulated and measured XPS spectra. Closer inspection of the XPS spectra reveals some differences between the calculated and experimental spectra, although several common features can be observed.

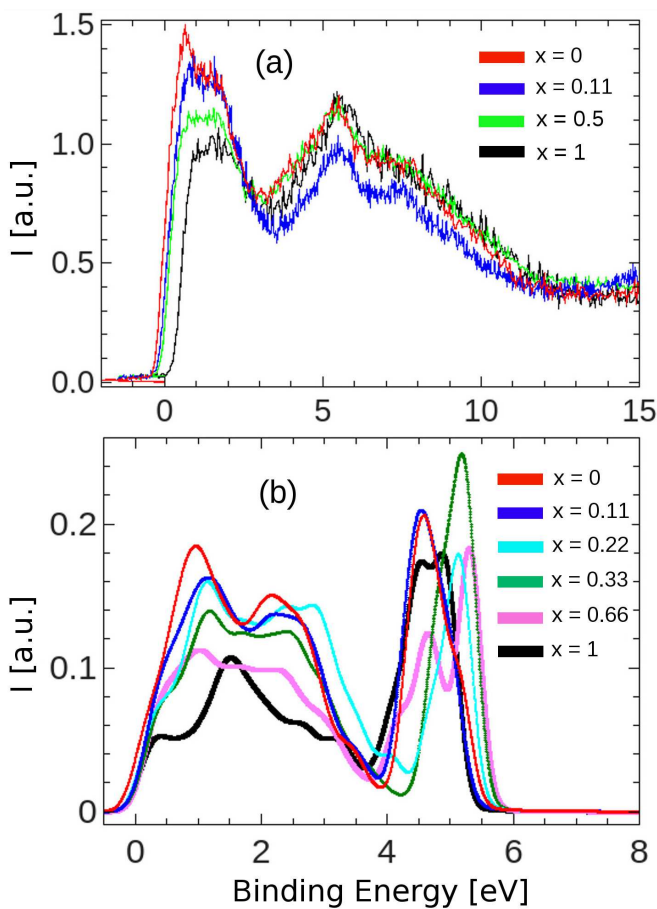


Fig. 3. Experimental (a) and theoretical (b) valence-band XPS spectra of the $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ alloys.

Location of the main VB peaks coincide in the both spectra. Furthermore, the changes of the calculated intensity of VB spectra upon Ni/Co replacement follows the observed ones. The comparison of calculated and experimental XPS spectra reveals however an opposite ratio between the VB and 4f intensities. The lower Sm-4f intensity than the VB one in experimental spectra may be

ascribed to the presence of the multiplet structure of 4f shell [17], visible as clearly separated peaks in 4f spectra (Fig. 3a). The splitting of the calculated Sm-4f sub-spectra is smaller than observed one. It results from the spin-orbit coupling and different value of chemical shift in Sm located at 3a and 6c positions.

To summarize, our results reveal the significant effect of the Ni/Co atom replacement on both the electronic structure and magnetic characteristics of $\text{Sm}(\text{Ni}_{1-x}\text{Co}_x)_3$ alloys. We found that variation of the magnetization of the alloys is driven by the *d* states of component atoms and increases roughly linearly with raising Co contents. Our calculations explain the essential features of the measured XPS spectra.

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