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# Effects of M=Si, Ga and Al for Co substitution on the electronic properties of $RCo_4M$ as probed by XPS

A. Laslo [a,b,c], R. Dudric [a], M. Neumann [d], O. Isnard [b], M. Coldea [a], V. Pop [a,*]

[a] Babes-Bolyai University, Faculty of Physics, 400084 Cluj-Napoca, Romania
[b] Univ. Grenoble Alpes, Inst NEEL, F-38042 Grenoble, France
[c] CNRS, Inst NEEL, rue des martyrs, B.P. 166, F-38042 Grenoble, France
[d] University of Osnabrück, Fachbereich Physik, 49069 Osnabrück, Germany

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ABSTRACT

The electronic properties of $RCo_{5-x}M_x$ (R=Er, Sm, Tm; M=Si, Ga, Al; $x$=0 and 1) compounds were investigated by X-ray photoelectron spectroscopy (XPS). The study was focused on the Co 3s exchange splitting, the valence bands and chemical shifts of the elements from the analyzed compounds. The Co $2p_{3/2}$ core-level chemical shifts were described by means of the Auger parameters and Wagner plot. The hybridization between the R 5d6s and M 3sp and 4sp states and Co 3d states leads to a partial filling of the Co 3d band and to a decrease of the Co magnetic moments in comparison with the value in pure Co metal, in good agreement with the magnetic measurements.



## 1. Introduction

X-ray photoelectron spectroscopy (XPS) has been proved to be of considerable importance in the understanding of the magnetic properties and electronic structure of the rare earth (R)–transition metal (T) compounds [1,2]. The correlation of the data obtained from XPS spectra and magnetic measurements gives information on the 3d and 4f electronic states, the degree of localization/delocalization of the 3d electrons, the charge transfer between the constituent elements, the hybridization between the 3d states and sp states from outer shells of the neighboring atoms, the effect of vicinity on the magnetic moments. In metallic systems based on 3d transition elements the main contribution to the valence band is due to the 3d electrons [3,4]. The position of the Fermi level ($E_F$) and the slope of the valence band spectrum in the vicinity of the Fermi level represent a measure of the unoccupied 3d states and of the density of states N ($E_F$), respectively [5]. The exchange splitting of the 3s core level is a direct evidence of the local magnetic moment on the transition element sites [1,6]. The chemical shits of the core levels from different components of the analyzed compound reflect the changes in the electronic structure of the atoms produced by alloying [7].

The compounds $RCo_5$ have been intensively studied both for their remarkable magnetic properties and multiple technological applications [8–12] in particular as high temperature permanent magnets. It was shown that the partial substitution of Co by M=Al, Ga and Si preserves the $CaCu_5$ structure type of the parent compounds [13,14] even if the lattice parameters slightly evolved being larger for Al and Ga and smaller for Si containing phases. It has been shown that significant changes occur in the magnetic properties of the $RCo_{5-x}M_x$ compounds both at the macroscopic level (magnetization, transition temperature) and at the microscopic level (atomic magnetic moments, electronic structure, anisotropy) in comparison with the $RCo_5$ compounds [15–23]. Large decrease of the Curie temperature has been reported upon partial substitution M=Al, Ga and Si for Co. More recently large enhancement of the magnetocrystalline anisotropy has been reported for $SmCo_{5-x}M_x$ compounds (M=Al, Ga) [16]. Consequently, the changes of the electronic properties have attracted interest among the last few years.

The aim of this paper is to reveal, through XPS measurements, the changes in the electronic properties of the $RCo_{5-x}M_x$ relative to the parent compounds $RCo_5$. The study will be focused on the magnetism of Co atoms, taking into account the sensibility of Co magnetic moment on the atomic vicinity, in particular on the hybridization of 3d states with the sp states of neighboring M atoms, the concentration of electrons and the magnetic interactions present in the system.

* Corresponding author. Tel.: +40 746 201 051.
*E-mail address:* viorel.pop@phys.ubbcluj.ro (V. Pop).

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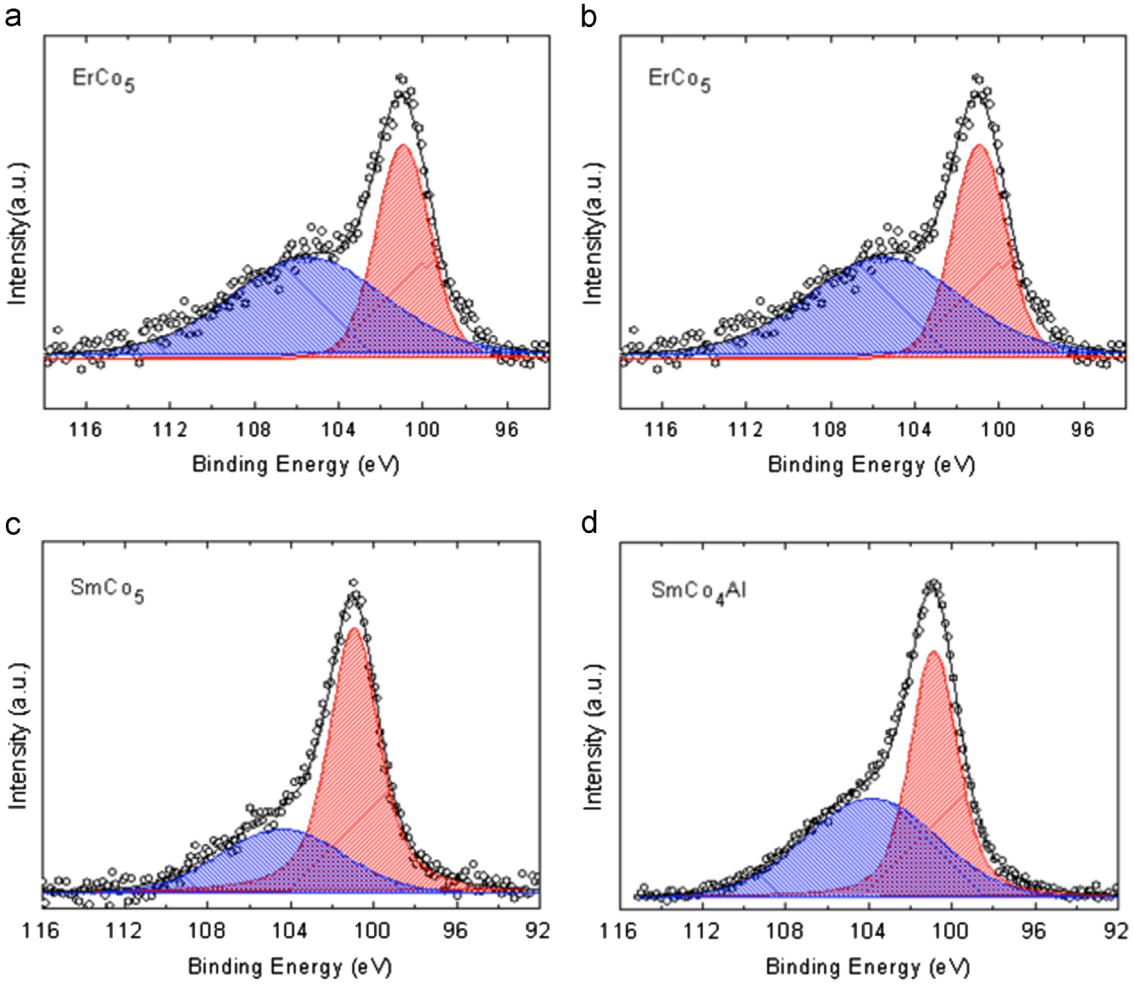


**Fig. 1.** (Color online) XPS spectra of the Co 3s core levels in $ErCo_5$ (a), $ErCo_4Si$ (b), $SmCo_5$ (c) and $SmCo_4Al$ (d) compounds (open circles correspond to the experimental spectra and the continuous curves to the fitting results).

## 2. Experimental

The compounds $RCo_{5-x}M_x$ (R=Sm, Er, Tm; M=Si, Ga, Al; $x$=0 and 1) were prepared in a cold crucible induction furnace under a purified argon atmosphere. The samples were melted repeatedly in the same atmosphere to ensure homogeneity. The purity of the starting materials was 99.95% for R and M elements and 99.5% for Co. The crystalline structure of the samples was analyzed at room temperature using a Siemens D5000 diffractometer with Cu Kα radiation. The X-ray diffraction data have shown that all the samples are single phases with the $CaCu_5$ structure type. The XPS spectra were recorded using a PHI 5600ci ESCA spectrometer with monochromatized Al Kα radiation at room temperature. The pressure in the ultrahigh vacuum chamber was in the $10^{-10}$ mbar range during the measurements. The ingot samples were cleaved in situ and the surface cleanness was checked by monitoring the O 1s and C 1s core levels in the survey spectra.

After Ar ion sputtering at low energies for ten minutes, the intensities of the O 1s and C 1s core levels were low, indicating a negligible contamination.

## 3. Results and discussions

The Co 3s core level spectra for all investigated compounds show an exchange splitting arising from the exchange interactions between the core hole and the open 3d shell. This is a direct evidence of the local magnetic moments on Co sites. The exchange interaction $J_{dc}$ between the core hole spin $s$ and the 3d electron spin $S$ gives rise to a satellite on the high binding energy of the main line of the Co 3s spectrum. In Fig. 1 are shown the curve fitting results of Co 3s spectra for $ErCo_5$ (a), $ErCo_4Si$ (b), $SmCo_5$ (c) and $SmCo_4Al$ (d) compounds, after background subtraction of Shirley type [24]. Similar spectra were obtained for $ErCo_4Ga$ and $SmCo_4Ga$. It is to be noticed that the deconvolution of the Co 3s spectra in $ErCo_4Ga$ and $SmCo_4Ga$ compounds was done taking into account the superposition of the Co 3s and Ga 3p spectra. For all Er compounds it was necessary to subtract also the Auger line observed at 98.7 eV

**Table 1**
The exchange splittings of Co 3s core levels in $RCo_{5-x}M_x$ (R=Er and Sm; $x$=0 and 1).

| Compound | $ErCo_5$ | $ErCo_4Ga$ | $ErCo_4Si$ | $SmCo_5$ | $SmCo_4Ga$ | $SmCo_4Al$ |
|---|---|---|---|---|---|---|
| $\Delta E_{ex}$ (eV) | 4.5 | 3.1 | 3.1 | 3.5 | 3.0 | 3.0 |

The two peaks in the deconvolution of the Co 3s spectra correspond to the high spin final state ($S+1/2$) and the low spin final state ($S-1/2$), respectively. The exchange splitting $\Delta E_{ex}=J_{dc}(2S+1)$ has been reported to be proportional with the Co magnetic moment $\mu_{Co}=2S$ [25]. The values of the exchange splitting for all investigated compounds are given in Table 1. The exchange splitting in $ErCo_5$ is close to that found in the pure Co