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Electronic structure and magnetic properties of the $HoCo_{5-X}Si_x$ system

D. BENEA[a], O. ISNARD[b,c], N. COROIAN[a,b], V. POP [a*]
[a]*Babes Bolyai University, Faculty of Physics, 400084 Cluj-Napoca, Romania*
[b]*Institut Néel, CNRS, associé a Université Joseph Fourier, BP166, 38042 Grenoble cedex, France*
[c]*Institut Universitaire de France, Maison des Universites, 103 Boulevard Saint Michel, 75005 Paris cedex, France*

Detailed theoretical and experimental investigations of the electronic and magnetic properties of the $HoCo_{5-x}Si_x$ compound (x = 0.5 and 1.0) have been performed. All theoretical investigations of the electronic and magnetic properties of the system have been done using the Korringa-Kohn-Rostoker (KKR) band structure method. The calculated magnetic moments range between 1.36 to 1.5 μ_B per Co atom, depending on the crystal site. The calculations show a spin and orbital moment of Ho of 3.85 μ_B and 5.46 μ_B, respectively, oriented antiparallel to the Co moments. These results are in reasonable agreement with macroscopic saturation magnetisation.

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1. Introduction

Intermetallic compounds of 4f elements and cobalt atoms have attracted considerable attention for many years for their technological applications as well as from the viewpoint of basic research [1-5]. The combination of rare earth and Co atoms can give rise to materials exhibiting high Curie temperature, given by the strong exchange interaction between the 3d electrons of Co, and a strong anisotropy provided by the rare earth 4f electrons. The replacement of Co in RCo_5 compounds by non-magnetic p-elements such as B, Al, Ga or Si has a strong impact on the crystallographic and magnetic properties of the host compounds [6-14]. The hexagonal crystal structure of $CaCu_5$ type is conserved as in RCo_5 compounds for Al, Ga and Si substitution. Co atoms occupy two different crystallographic sites in the $CaCu_5$ type of structure: 2c –in the basal plane with the R atoms and 3g– in a plane containing only Co atoms ($z = c/2$ plane). The smaller radius of B leads to a preferential substitution of B for Co in the 2c site forming the $R_{n+1}Co_{5+3n}B_{2n}$ series (n = 0, 1, 2, …) with space group symmetry P6/mmm [13, 15, 16]. The preferential occupation of either 2c or 3g crystallographic positions of Co by p-elements in the $CaCu_5$ hexagonal structure of the $RCo_{5-x}M_x$ compounds has been explain taking into account both affinity and size effect [10-14, 17] .

The magnetic properties in the $RCo_{5-x}M_x$ intermetallic compounds are strongly related to the nature of the rare earth element and of the substituting p-element. The Si substitution in the RCo_5 compounds does not change the type of magnetic ordering: ferromagnetic for R = Y, Nd or Pr and ferrimagnetic for heavy rare earth (Gd, Tb, Dy, Ho and Er) but strongly modifies the other magnetic properties. The most striking effects have been found on the exchange interaction and the magnetocrystalline anisotropy of both R and Co sublattice, respectively [18, 19]. The Curie temperature and the magnetic moments of Co atoms strongly decrease by Si substitution in the RCo_5 compounds [6, 7, 20, 21]. The weaker Co-Co exchange interactions may be the consequence of the hybridization between the 3d-states of Co and the 2p states of Si.

In this paper we report on the influence of the Si for Co substitution on the electronic band structure in the $HoCo_{5-x}Si_x$ compounds. The magnetic moments of Co atoms, the easy magnetization direction (EMD), as well as the stability of the possible crystal structures at low temperature are discussed in the following.

2. Computational details

The electronic structure of the $HoCo_{5-x}Si_x$ has been calculated self-consistently by means of the spin-polarized relativistic Korringa-Kohn-Rostocker (SPR-KKR) band structure method in the atomic sphere approximation mode [22-24]. The calculation method is based on the KKR Green's function formalism and makes use of the multiple scattering theory. The details of the calculations have been described elsewhere [25, 26]. The local spin density approximation (LSDA) for the exchange-correlation energy using the Vosko, Wilk and Nusair parameterization was used [27]. The computations were done for 301 k-points in the irreducible wedge of the first Brillouin zone. For integration over the Brillouin zone, the special points method has been used [28]. The substitutional disorder in the system has been accounted for by means of the Coherent Potential Approximation (CPA) [23, 29]

3. Results and discussions

The X-ray diffraction experiments performed at 300 K show that the structure of $HoCo_{5-x}Si_x$ is of $CaCu_5$ type, belonging to the space group P6/mmm. The experimental details have been described elsewhere [6, 7]. Within this structure, the Ho atoms occupy the *1a* (0, 0, 0) positions and the Co atoms occupy the *2c* (1/3, 2/3, 0) and *3g* (1/2, 0, 1/2) positions. Neutron diffraction experiments [6] have been performed in order to determine the preferential occupation of Si atoms by substitution of Co atoms. The experiments show that the Si for Co substitution takes place exclusively on the *3g* crystallographic site. This result is in agreement with the variation of the lattice parameters with Si content (Table 1) which evidence that the *a* parameter is almost constant whilst the *c* parameter, governed by the size of the atom sitting on the *3g* site, decreases with the Si content.

Table 1. *Lattice parameters of the $HoCo_{5-x}Si_x$ compounds[6].*

compound	Cmmm (4K)				P6/mmm (300 K)	
	a'(Å)	b'(Å)	c'(Å)	a(Å)	c(Å)	V(Å ^{3})
$HoCo_5$	-	-	-	4.911	3.993	83.401
$HoCo_{4.5}Si_{0.5}$	4.878	4.902	3.953	4.915	3.965	82.937
$HoCo_4Si$	4.908	4.922	3.927	4.922	3.928	82.411

The crystal structures of the $HoCo_{5-x}Si_x$ compounds have been determined at different temperatures from neutron diffraction patterns [6]. For both $HoCo_{4.5}Si_{0.5}$ and $HoCo_4Si$ compounds a reduction of the crystal symmetry described by an orthorhombic Cmmm structure under ~150 K has been observed

This transition is determined by a shift of the atomic position occupied by Co within the ab plane.

The correspondence between the occupation of the crystallographic sites of the Cmmm and P6/mmm structures is described in Table 2. The *4g* crystallographic position is (x, 0, 0), which for the ideal $CaCu_5$ structure is (2/3, 0, 0). The deviation of x from 2/3 shows that the structure is not anymore of $CaCu_5$ type but can be described by the Cmmm space group.

Table 2. *Atomic positions in the $CaCu_5$ structure described by the Cmmm space group (x = 0.33 or 0.66) and the correspondence between the site occupation of both representations.*

	Cmmm		P6/mmm	
atoms	site	positions	site	positions
Ho	*2a*	(0, 0, 0)	*1a*	(0, 0, 0)
Co	*4g*	(x, 0, 0)	*2c*	(1/3, 2/3, 0)
Co + Si	*4f*	(1/4, 1/4,1/2)	*3g*	(1/2, 0, 1/2)
	2c	(1/2, 0, 1/2)		

For all $HoCo_{5-x}Si_x$ compounds a ferrimagnetic behaviour has been found [4]. The temperature dependence of the magnetization shows that for $HoCo_5$ compound there is compensation between the magnetic lattices at 159 K, but the compensation is not entire, showing that the magnetic networks are not collinear. The $HoCo_5$ compound exhibits also a spin reorientation at 180 K, the magnetization being axial above this temperature and conical spin orientation below this temperature, respectively [4].

The saturation of magnetization at 4 K is shown in Table 3. The average magnetic moment of Co was determined from the experimental data, considering that Ho has the same magnetic moment as Ho^{3+} ion (10 μ_B/atom). As can be seen in Table 3, the magnetic moments decrease with Si content as a consequence of diminishing of the Co-Co exchange interactions. As a comparison, Thang et al. [20] found for $HoCo_4Si$ compound a similar saturation magnetization of 5.08 (μ_B/f.u.) and the Curie temperature of 420 K.

Fully relativistic SPR-KKR band structure calculations have been performed for the $HoCo_{5-x}Si_x$ compounds in hexagonal P6/mmm and orthorhombic Cmmm type of structure using the experimental lattice parameters. The lattice parameters for P6/mmm type of structure have been extrapolated at low temperature, close to 0 K.

Table 3 *The 4K spontaneous magnetization and the mean Co magnetic moments deduced for the $HoCo_{5-x}Si_x$ [4, 6, 30].*

Compound	$HoCo_4Si$	$HoCo_{4.5}Si_{0.5}$	$HoCo_5$
M_s (μ_B/f.u.)	5.38	2.92	1.1
μ_{Co}(μ_B)	1.16	1.57	1.78

The band structure calculations show that, for these compounds, the orthorhombic Cmmm structure is more stable than hexagonal one. In order to determine the most stable spin configuration of the $HoCo_{5-x}Si_x$ compounds, the total energy of the systems has been calculated. The magnetization direction has been considered along the c axis and in ab plane, respectively. The calculations show that the most stable spin configuration at low temperature is the orthorhombic Cmmm structure with the magnetization within the basal plane, in perfect agreement with the neutron diffraction data.

The SPR-KKR fully relativistic band structure calculations have been performed for the $HoCo_{5-x}Si_x$ compounds (x = 0.5, 1.0) in Cmmm type of structure with the experimental lattice parameters [6]. The spin and component resolved densities of states (DOS) for $HoCo_{4.5}Si_{0.5}$ compound are presented in Fig. 1. One should note that the partial DOS of each component is weighted by number of atoms in the unit cell in order to get the total DOS. The origin of the energy scale is the Fermi level, E_F. The higher energy band crossing the Fermi level has pronounced Co 3d and Ho 4f character. Si contribution to DOS is small because of the small number of electrons provided to the valence band. The larger magnetic moment is obtained for the Co 4f and 2c sites whereas a significantly lower magnetic moment is found on the Co *4g* site. The observed difference in the exchange-splitting plays in favour of the different magnetic moments on Co *2c, 4f* and *4g* sites. For the $HoCo_4Si$ compound the larger Co moment is even observed on the Co 2*c* sites. As can be seen from Fig. 1 the band structure of the inequivalent Co sites are different in shape. This is noticeable at the Fermi level but also at lower energies where the hybridization with the Si atoms induces a significant DOS broadening. The broadening of the bands of Co up to around 10 eV binding energy indicates a hybridization of d states of Co with the s and p states of Si. According to the DOS plotted in Fig. 1, there is a strong hybridization between the 3d (Co) – p (Si) electronic states whose contributions to the DOS are mostly above -6 eV.

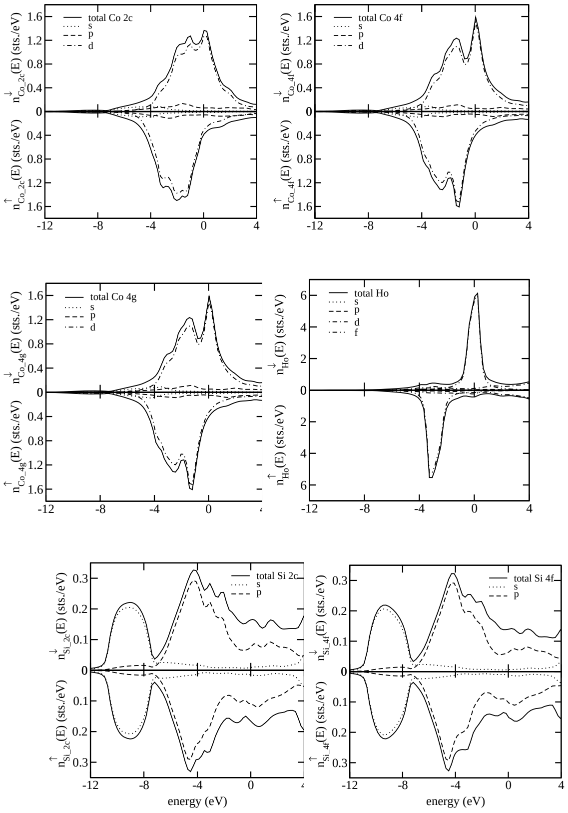

***Fig. 1** Spin and component resolved density of states for $HoCo_{4.5}Si_{0.5}$ compound.*

Very similar in shape DOS has been obtained for $HoCo_4Si$. Lower exchange coupling, DOS at E_F and slightly higher bands width has been observed [31]. The Si substitution cause charge transfer between ions: from Si to Co and Ho atoms. Electron transfer to Co atoms fills the 3d band and reduces their magnetic moments, as will be shown below.

The magnetic moments for ferrimagnetic $HoCo_{5-x}Si_x$ compounds in orthorhombic Cmmm structure, obtained by SPR-KKR band-structure calculations with the magnetization within the *ab* plane are presented in Table 4. Indeed, comparisons of the band structure calculations performed with a spin orientation along the *c* axis or in the basal plane reveal that the lower energy configuration corresponds to the basal plane orientation. This confirms the possibility of a spin reorientation phenomenon in these compounds since the Co magnetic sublattice is known to favour the *c* axis in the RCo_5 type compounds. One should emphasize the good agreement between the SPR-KKR calculated magnetic moments and the experimental measurements for saturation of magnetization (Table 3) and neutron diffraction for $HoCo_{4.5}Si_{0.5}$ [32]. As can be seen in Table 4, the magnetic moments of Co decrease with increasing the Si content of the compounds. Similar behaviour was observed also by Szajek et al. for $GdCo_4Al$ in hexagonal P6/mmm structure [33]. It is worth to note that the magnitude of the Co magnetic moment is significantly reduced in comparison to the 1.8 μ_B generally reported for the RCo_5 parent compounds [4]. This reflects at a microscopic scale the large influence of the Si for Co substitution on the magnetic properties. The calculated Co moments are in good agreement with the one deduced from the saturation magnetisation reported in Table 3. As expected the Co magnetic moment mainly originates from spin. The orbital contribution is an order of magnitude smaller. It is remarkable that the Co 2c exhibits by far the largest orbital moment 0.13 μ_B against to 0.08 to 0.09 μ_B for the Co 4g and 4f site respectively, Table 4.

The calculated Ho magnetic moment was smaller than the free ion value: 10.6 μ_B for Ho^{3+}. This discrepancy slightly increases with increasing the concentration of Si atoms and displays important role of Si – 2p electrons in hybridization effects. Also, as it was shown by Brooks et al. [34, 35], the 5d electrons of the rare earth atom play a key role in the rare earth – transition metal coupling, the indirect 4f-3d interactions are involving intra-atomic 4f-5d exchange, and interatomic 3d-5d exchange interactions. The systematic analysis of the magnetic properties of rare earth –3d transition metal based compounds reveal that the variable degree of 3d-5d hybridization essentially determines the variations in the 3d-4f exchange. The calculations show that the 5d magnetic moment of Ho decrease with Si content (from 0.18 μ_B/atom in $HoCo_{4.5}Si_{0.5}$ to 0.14μ_B/atom in $HoCo_4Si$). Thus the contribution coming from 3d-5d interaction is diminished by Si substitution. As can be expected from the polarisation of Si electronic state by the Co 3d spins leads to a small induced magnetic moment oriented parallel to the Ho magnetic moment.

***Table 4.** SPR-KKR calculated magnetic moments in $HoCo_{5-x}Si_x$ compounds (x = 0.5, 1.0).*

M || *ab*	$HoCo_{4.5}Si_{0.5}$ –Cmmm structure			$HoCo_4Si$ - Cmmm structure		
	m_{spin} (μ_B)	m_{orb} (μ_B)	m_{tot} (μ_B/f.u.)	m_{spin} (μ_B)	m_{orb} (μ_B)	m_{tot} (μ_B/f.u.)
Ho (*2a*)	-3.85	-5.46	-9.33	-3.80	-5.44	-9.24
Co (*4f*)	1.39	0.09	1.48	1.07	0.08	1.15
Si (*4f*)	-0.07	0.00	-0.07	-0.05	0.00	-0.05
Co(*2c*)	1.37	0.13	1.50	1.13	0.12	1.25
Si(*2c*)	-0.07	0.00	-0.07	-0.05	0.00	-0.05
Co(*4g*)	1.27	0.08	1.35	0.95	0.08	1.03
M_s			-3.19			-4.86

4. Conclusions

Band structure calculations performed for $HoCo_{5-x}Si_x$ compounds confirm the experimental results showing that the most stable structure at low temperature is the orthorhombic Cmmm structure with ferrimagnetic spin configuration within the (a,b) plane. The most stable spin structure is determined by the competition between the Co and Ho anisotropies. The Ho anisotropy is dominant at low temperature and aligns the magnetic moments perpendicular to the c axis whereas a spin reorientation occurs at higher temperature.

The densities of states calculations reveal differences in exchange-splitting on Co sites, depending on the preferential site occupation of Si at substitution of Co. Also, exchange-splitting and DOS at E_F depend on the Si content of the compounds, showing that Co 3d –Si 2p hybridization is responsible for the reduction of the Co magnetic moments at Si for Co substitution. Another evidence of the Co 3d – Si 2p hybridization is the increase of the Co valence band broadening with increasing the Si content of the compounds.

The calculated total magnetic moments for $HoCo_{4.5}Si_{0.5}$ and $HoCo_4Si$ show a very good agreement with the spontaneous magnetization determined experimentally for both compounds.

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*Corresponding author: viorel@phys.ubbcluj.ro