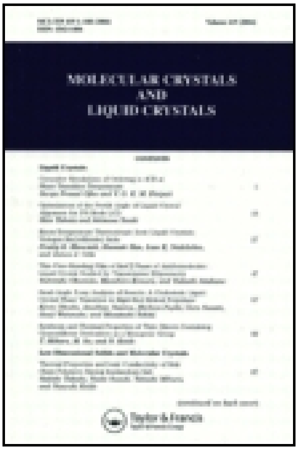

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E. Burzo [a] , C. Lazar* [a] , I. Balasz [a] & P. Vlaic [a]
[a] Babes-Bolyai University, Cluj Napoca, Romania

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MAGNETIC PROPERTIES OF $HoNi_{5-x}Al_x$ COMPOUNDS

E. Burzo, C. Lazar, I. Balasz, and P. Vlaic*
Faculty of Physics, Babes-Bolyai University, 3400 Cluj Napoca, Romania

The $HoNi_{5-x}Al_x$ compounds crystallize in a $CaCu_5$ type structure for $x < 2$. For higher aluminium content, a $HoNi_{2.6}Ga_{2.4}$ type structure was shown. Band structure calculations show the presence of ordered nickel moments at 2c and 3g sites in $HoNi_5$. The nickel moments decrease when increasing aluminium content and is nil for $x \geq 1.5$. In paramagnetic range, the effective nickel moments decrease from $1.74\,\mu_B$ $(x = 0)$ to $1.30\,\mu_B$ $(x = 1)$ and $0.8\,\mu_B$ $(x = 2)$. The magnetic behaviour of nickel is analyzed in models which take into account the electron correlation effects in d-band.

Keywords: band structures; holmium compounds; spin fluctuations

1. INTRODUCTION

The RNi_5 compounds crystallize in a hexagonal structure of $CaCu_5$ type. The R atoms are located in 1a-type sites, while Ni occupies 2c and 3g positions [1]. Magnetic measurements performed on the above compounds show that the Curie temperatures T_C are very low. The maximum value $T_C = 35\,K$ was evidenced in $GdNi_5$. Generally, in earlier studies it was suggested that nickel is not magnetic in RNi_5 compounds [1]. Analyzing the magnetic properties of $Gd_xY_{1-x}Ni_5$ [2] and $Gd_xLa_{1-x}Ni_5$ [3] it has been shown that Ni 3d band is polarized and that the mean nickel moments decrease gradually from $\sim 0.17\,\mu_B$ for $x = 1.0$ and is nil in $LaNi_5$ or in YNi_5.

In pseudobinary $RNi_{5-x}Al_x$ with R = Nd, Gd, Dy [4–6] the crystal structure changes from $CaCu_5$ type to $HoNi_{2.6}Ga_{2.4}$type for $x \geq 2$. In $CaCu_5$-type structure, the aluminium substitution takes place only at the 3g site, situated in the $z = 1/2$ plane which does not contain R atoms. These sites allow greater Ni-Al distances. The total filling of the 3g site is not possible since

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*Corresponding author. Tel.: 0264 405300 int. 5151, E-mail: clg@gmx.net the distances between 3g-3g or 2c-3g sites, for x > 2, are smaller than the sum of metallic radii $r_{Ni} + r_{Al}$ or $r_{Al} + r_{Al}$ [4]. The occurrence of $HoNi_{2.6}Ga_{2.4}$ superstructure induces an increase in the distances between Al(3f)-Ni(6k) making possible to locate aluminium in the 3f and 6k sites.

In this paper we report the crystal structure and magnetic properties of $HoNi_{5\text{-}x}Al_x$ compounds. The experimental data were analyzed in correlation with computed band structures.

2. EXPERIMENTAL AND COMPUTING METHODS

The $HoNi_{5\text{-}x}Al_x$ compounds were prepared in an induction furnace in purified argon atmosphere. The samples were thermally treated in vacuum at ~1000°C for one week. The X-Ray analyses show the presence of only one phase. The compounds with $x \leq 1.5$ were indexed on the basis of the hexagonal $CaCu_5$ type structure. For $x \geq 2$ compositions, a $HoNi_{2.6}Ga_{2.4}$-type structure was shown. The lattice parameters increase when aluminium content is higher – Table 1.

Magnetic measurements were performed in the temperature range of 1.7 (4.2)-300 K, in fields up to 9 T. Because of the low values of the Curie temperatures, $T_C \leq 5\,K$, only the magnetization curve for $HoNi_5$ at 1.7 K was analyzed. Even in this case the ratio T/T_C is 0.3 and does not reflect the saturation magnetization at 0 K. In the paramagnetic range, the magnetic susceptibilities, χ, were determined from their field dependencies, according to the relation $\chi_m = \chi + bM_sH^{-1}$, by extrapolating the measured values χ_m at $H^{-1} = 0$. We denoted by χ_m the measured magnetic susceptibility, b is a presumed magnetic ordered impurity content having saturation magnetization, M_s. By this method any possible alteration of magnetic susceptibility as a result of the presence of small quantities of

TABLE 1 Crystal Structure and Lattice Parameters for $HoNi_{5\text{-}x}Al_x$ Compounds

		Lattice parameters (Å)	
Composition	Structure	a	c
x = 0	$CaCu_5$	4.8732	3.9625
x = 0.5	$CaCu_5$	4.8937	4.0024
x = 1	$CaCu_5$	4.9225	4.0345
x = 1.5	$CaCu_5$	4.9824	4.0565
x = 2	$HoNi_{2.6}Ga_{2.4}$	8.7913	4.05316
X = 3	$HoNi_{2.6}Ga_{2.4}$	8.9401	4.0720

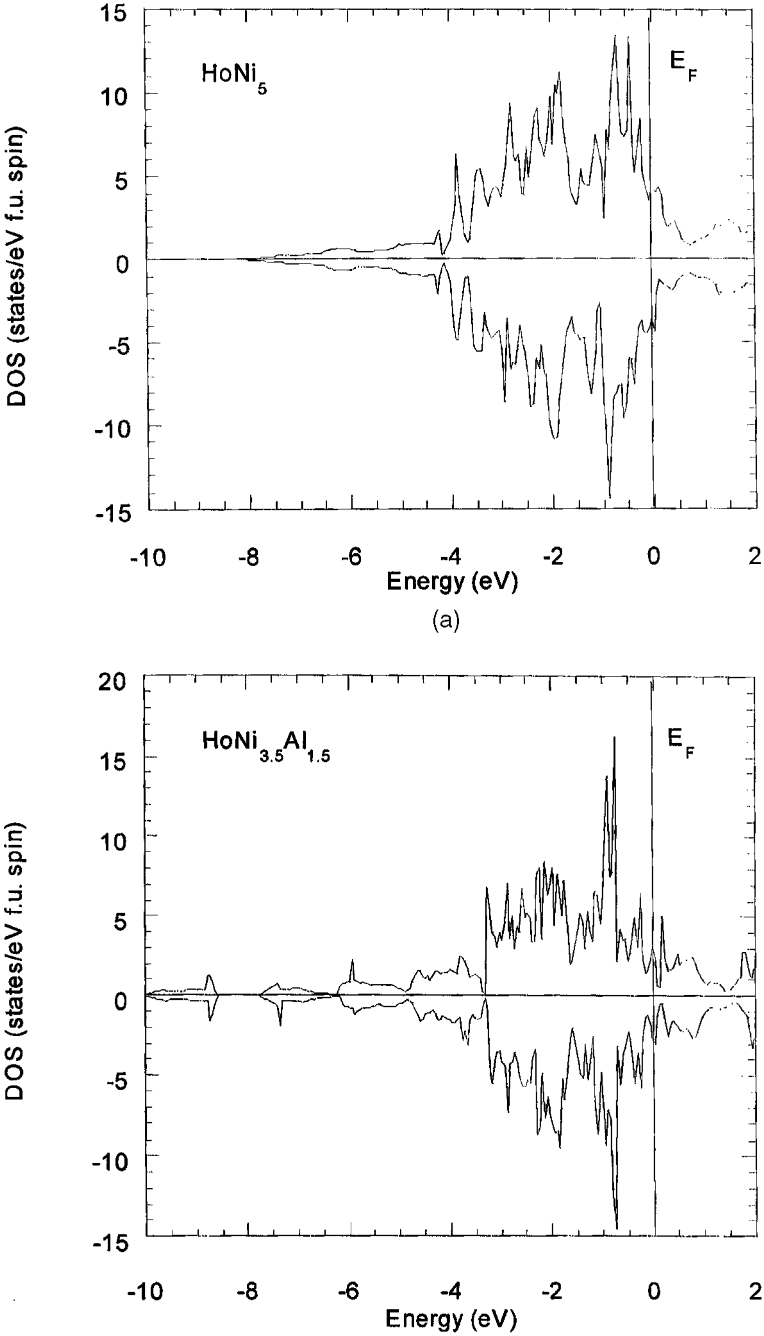
magnetic ordered phase is avoided. For all compositions, the estimated content of magnetic ordered phase, at $T > Tc$, when exists, is smaller than 0.1%.

Band structure calculations were carried out by using the ab initio tight binding linear muffin tin orbital method in the atomic sphere approximation. The detailed procedure of calculation is described elsewhere [7,8]. In the framework of the local density approximation (LDA), the total electronic potential is the sum of the external- Coulomb and exchange correlation potentials [9]. The frozen core approximation was applied in the generation of the potential and the parametrization of von Barth and Hedin [10] was used for the exchange correlation part of the effective electron potential, obtained within the local spin density approximation of the density functional theory. For the band structure calculation, in $CaCu_5$-type structure the Al was introduced in 3g sites. All calculations were performed using the experimentally determined lattice constants.

3. BAND STRUCTURE

The total density of states (DOS) for $HoNi_{5-x}Al_x$ compounds with $x \leq 1.5$ are plotted in Figure 1. The magnetic moments at 2c and 3g sites are 0.14 μ_B/atom and 0.22 μ_B/atom, respectively antiparallel oriented to holmium moment. The moments at Ni (3g) sites are higher than those at 2c sites. This behaviour may be attributed to different local environments. The 2c site in $HoNi_5$ has 6 Ni (3g) and 3 Ni (2c) atoms, as well as 3 Ho ones, while 3g site has 4 Ni (2c), 4 Ni (3g) and 4 Ho as nearest neighbours. The strength of exchange interaction between Ni and Ho is more important than between those of Ni, the Ni moments being essentially induced by the presence of magnetic Ho atoms. The compound is ferrimagnetically ordered. The Ho 5d band polarization is parallel to the Ho 4f moment, $M_{5d} = 0.144\,\mu_B$. Thus, analyzing the balance between magnetic moments, we conclude that the total contribution of nickel to the magnetization is smaller than $\sim$8% from the Ho moment. Consequently, this contribution is difficult to be determined by magnetic measurements in RNi_5 compounds with non-S state rare-earth, because of rather high anisotropy and difficulties in obtaining the saturation.

When replacing Ni by Al, the nickel moment, determined from band structure calculations, decreases. Thus for $x = 1.0$ values of $M_{Ni}(2c) = 0.05\,\mu_B$/atom and $M_{Ni}(3g) = 0.10\,\mu_B$/atom were determined. For compounds $x \geq 1.5$ the nickel moment is essentially nil. The above data suggest a transition from a ferrimagnetic type ordering to a ferromagnetic one when increasing aluminium content.



(a)

(b)

FIGURE 1 Band structures of $HoNi_{5-x}Al_x$ compounds with $x = 0$ and $x = 1.5$.

4. MAGNETIC MEASUREMENTS

The Curie temperature of HoNi$_5$ is ~5 K [1] and decreases when increasing aluminium content. The magnetization isotherm obtained at 1.7 K evidences a magnetic moment, at 9 T, of ~8.7μ_B/f.u. If the determined values were extrapolated to infinite field according to the relation $M = M_S$ (1-a/H), the value of 9 μ_B/f.u. was obtained. This is somewhat smaller than that corresponding to Ho metal $g_J J = 10\,\mu_B$/f.u. If we consider the contributions of Ho 5d, Ni (2c) and Ni (3g) to magnetization, the value of 9.1μ_B/f.u. is expected, close to that experimentally determined. Because of the low Curie temperatures no reliable data concerning the saturation magnetizations may be obtained for Al substituted compounds.

In paramagnetic range, the reciprocal susceptibilities (Fig. 2) follow a Curie-Weiss behaviour. The Curie constants are somewhat higher than that of Ho^{3+} ion suggesting an additional contribution from nickel atoms. According to the addition law of the magnetic susceptibilities we determined the contributions of nickel to the Curie constants and effective nickel

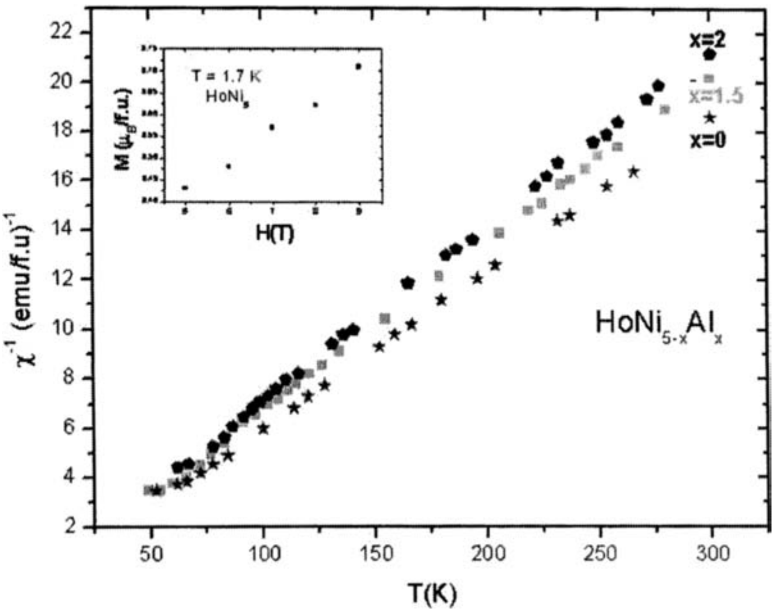


FIGURE 2 Thermal variations of reciprocal susceptibilities for HoNi$_{5\text{-}x}$Al$_x$ compounds. In inset the magnetization curve for HoNi$_5$ is plotted.

moments, respectively. The effective nickel moments decrease from 1.74 μ_B ($x = 0$) to $0.80\mu_B$ ($x = 2$).

5. DISCUSSION

The band structure calculations and magnetic measurements show that $HoNi_5$ is ferrimagnetically ordered, nickel at 0 K having a small magnetic contribution. By increasing the aluminium content the nickel moments decrease and are nil for $x \geq 1.5$. In paramagnetic range an effective nickel moment was shown, which decreases when increasing Al content. The above magnetic behaviour of nickel may be analyzed by considering models which take into account the electron correlation effects in the d-band as the spin fluctuation model [11,12] or dynamical mean field theory [13]. These models reconcile the dual character of the electron, which as a particle requires a real space description and as a wave, a momentum space description. The spin fluctuation model considers the balance between the frequencies of longitudinal spin fluctuations, which are determined by their lifetime and of transverse fluctuations that are of thermal origin. These effects lead to the concept of temperature induced moments. For a weak or nearly ferromagnet as Ni in $HoNi_{5-x}Al_x$ system, the wave number dependent susceptibility, χ_q, has a large enhancement due to electron-electron interaction for small q values. The χ_q shows a significant temperature dependence only for q values close to zero. The average amplitude of spin fluctuations $\langle S_{loc}{}^2 \rangle = 3k_B T \sum_q \chi_q$ increases with temperature and reaches an upper limit at a temperature T^*. For $T > T^*$ a Curie-Weiss behaviour is predicted, similar to a system having local moments. The moments are localized in q-space. In $HoNi_5$ the effective nickel moments are smaller than the value expected for Ni^{2+} ion (2.83 μ_B/atom). This decrease may be attributed to diminution of electron correlation due to 3d-5d hybridization. As a result, the spin fluctuations are not saturated and thus the value of 2.83 μ_B/atom cannot be attained. In addition, in Al-doped systems, there are also Ni 3d–Al 3p bands hybridizations. These lead to a gradual decrease of the effective nickel moment as the aluminium content increases. We note that in spin fluctuations model the effective Ni moments and those obtained at 0 K are not correlated [6].

The magnetic behaviour of nickel in $HoNi_{5-x}Al_x$ may be also analysed in the dynamical mean field theory (DMFT) combined with standard LDA band calculation (LDA + DMFT) [13,14]. In a strongly correlated system, a Curie-Weiss behaviour, at high temperatures, is predicted. For an itinerant electron system, the time dependence of the correlation function results in a temperature dependence of $\langle S_{loc}{}^2 \rangle$. Fluctuating moments and atomic like configurations are large at short time scales. The moment is reduced at larger time scales, corresponding to a more band like less correlated electronic structure near the Fermi level.

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