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On the electronic properties of $YCo_{5-x}Ni_x$

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Abstract

The magnetic and orbital moments of Co atoms in $YCo_{5-x}Ni_x$ were computed with the Haydock recursion method in a self-consistent procedure. The decrease in magnetic moment per formula unit with increase in Ni concentration is related to the peculiarities of the density of states for $x \neq 0$ and to the decrease in exchange splitting. The transition temperatures were computed in the framework of the spin-fluctuations theory. There are large orbital moments on both Co sites for all the compounds. The orbital polarization was considered as an effective spin-orbit interaction.

Keywords: Electronic properties; Cobalt; Orbital polarization

1. Introduction

Almost all rare earth elements can, together with Co atoms, form $CaCu_5$ structure-type compounds, which are very important mainly because of their favorable properties for technological applications. They can be treated as models for a number of general problems associated with the nature of exchange interactions and magnetocrystalline anisotropy. It is well known that in the RCo_5 compounds the magnetocrystalline anisotropy is very large [1]. Even in YCo_5, where the contribution comes only from the Co sublattice, the anisotropy field is one order of magnitude higher than in pure metallic Co. In an NMR study [2], the large anisotropy of the Co hyperfine field was associated with the anisotropy of the 3d magnetization. A polarized neutron study [3], has shown that the orbital contribution to the magnetic moments of Co atoms is large, and band structure calculations [4] showed that the orbital angular momentum anisotropy is strongly correlated to the anisotropy energy. However, the orbital angular momentum anisotropy depends on the band structure through the band filling, as proved by Daalderop *et al.* [4].

The Y–Ni compounds show a large variety of magnetic properties ranging from collective electron metamagnetism, as in Y_2M_{17}, to exchange enhanced Pauli paramagnetism in YNi_5 and ferromagnetism in Y_2Ni_7 and YNi_3. As the Y content increases, the Curie temperature and the 3d magnetic moment decrease [5]. These properties originate also from the band structure of these compounds, namely the filling of the Ni 3d bands with Y 4d electrons, and from the associated hybridization between 3d and 4d bands.

In this paper we compute the density of states (DOS) and related quantities for $YCo_{5-x}Ni_x$ ($x=0$, 1, 2 and 3) in the paramagnetic and ferromagnetic states. The orbital moments were calculated through the spin-orbit interaction in the limit of large orbital polarization.

2. The computational method

The DOS was computed using the Haydock recursion scheme, in the tight binding approximation. The transfer integrals are expressed in terms of two-center integrals:

$$(l_i l_j n) = N_{l_i l_j n}\left(\frac{\sqrt{S_i S_j}}{R_{ij}}\right)^{l_i+l_j+1}\sqrt{\Delta_{l_i}\Delta_{l_j}} \tag{1}$$

where S_i is the Wigner–Seitz radius of the atom located on site i, R_{ij} is the distance between i and j sites, Δ_{l_i} is the width of the l_i band and $n=\sigma$, π or δ [6].

The parameters used in this method were computed from the elemental atoms potential parameters Δ^0 and C^0, in the non-linear extrapolation scheme [7] (Table 1):

$$\Delta = \Delta^0\left(\frac{S}{S^0}\right)^{(\mathrm{d}\ln\Delta/\mathrm{d}\ln S)} \tag{2}$$

$$C = C^0 + \frac{\mathrm{d}C}{\mathrm{d}\ln S}\delta\ln S \tag{3}$$

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Table 1
The potential parameters for the $YCo_{5-x}Ni_x$ compound: Δ denotes the band width, C the band center (self-energy) and S the Wigner–Seitz radius; * values for elemental atoms

	Δ (Ry)			C (Ry)			S (a.u.)		
	This work	[7]	[8]	This work	[7]	[8]	This work	[7]	[8]
Y	0.029	0.028 *	0.083	0.079	0.070 *	0.138	3.705	3.728 *	3.473
Co	0.015	0.015 *	0.009	−0.121	−0.123 *	−0.217	2.567	2.570 *	2.370

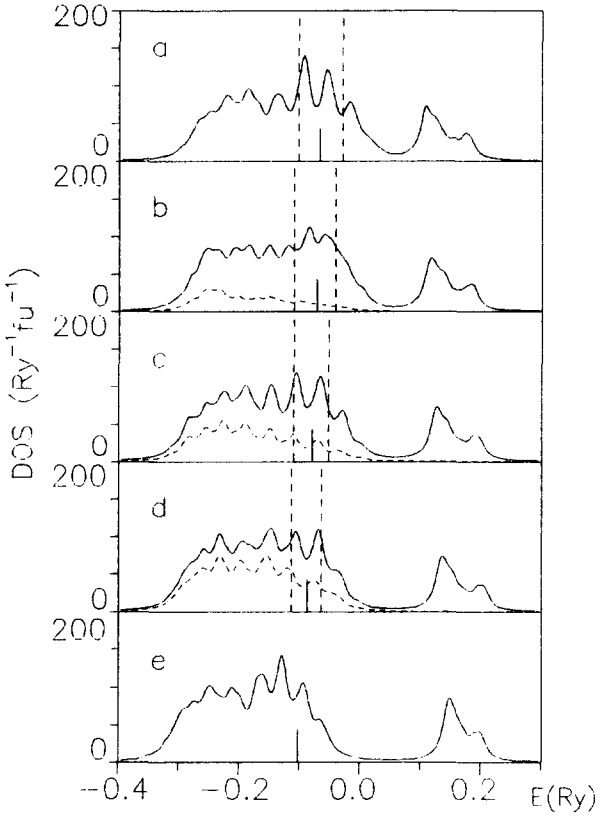

Fig. 1. The total DOS for $YCo_{5-x}Ni_x$ with $x=0$ (a), $x=1$ (b), $x=2$ (c), $x=3$ (d) and $x=5$ (e). The dashed curves show the Ni contribution to the total DOS. The short vertical line marks the paramagnetic Fermi level and the vertical dashed lines mark the Fermi level for the minority and majority spin bands.

The Wigner–Seitz radii of the atoms in compounds were found assuming a linear dependence of the atomic volume on the pressure.

The band width Δ was held constant during the computation and the C parameter was determined in a self-consistent procedure.

The magnetic moments were calculated by a rigid band splitting for up and down bands and the transition temperature in the framework of the spin fluctuations theory of Mohn and Wohlfarth [9] with the Stoner parameter used as an adjustable parameter.

The local orbital moments were calculated through the spin-orbit interaction. The up and down bands are shifted with an extra value of

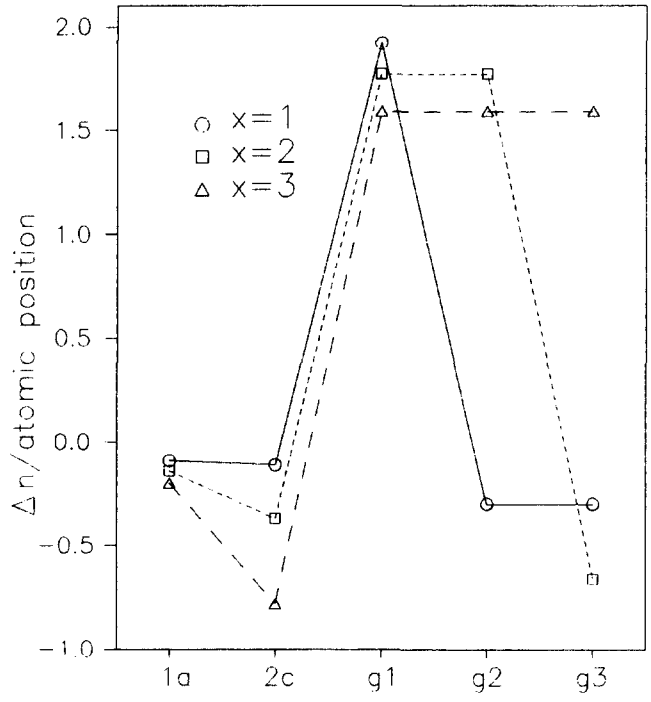

Fig. 2. The d-orbital occupation number variation Δn for $YCo_{5-x}Ni_x$ with respect to the YCo_5 compound at different atomic positions: 1a, 2c and 3g (g1, g2, g3).

$$\Delta E_s = (2l+1)\xi/2 \tag{4}$$

where ξ is the spin-orbit interaction parameter. The orbital moments were calculated using the formula [10]

$$m_l = g_l \mu_B \sum_{m=-2}^{m=2} m \int_{-\infty}^{\epsilon_F} \eta_l^m(\epsilon)\, d\epsilon \tag{5}$$

where η_l^m are the decomposed partial DOS of d electrons with azimuthal quantum number m [10–12].

The orbital moments on the Co sites are parallel to the spin moments, as was stated by Hund's third rule for the case of more than half-filled shells.

3. Results and discussions

The YCo_5 intermetallic compound crystallizes in the hexagonal $CaCu_5$ structure with lattice parameters $a=4.938$ Å and $c=3.981$ Å, as determined by Taylor

Table 2
The values of the spin, orbital and total (average $\bar{m}$ and local (2c and 3g positions)) magnetic moments for $YCo_{5-x}Ni_x$ as a function of x, expressed in μ_B per atom

	x	Spin	Orbital	Total	Reference
$\bar{m}$	0	1.38	0.09	1.47	This work
		1.34	0.12	1.46	[8]
				1.36	[20]
				1.65	[21]
				1.50	[22]
	1	1.15	0.08	1.23	This work
				1.35	[22]
	2	0.79	0.06	0.85	This work
				1.05	[22]
	3	0.50	0.05	0.55	This work
				0.44	[21]
				0.438	[22]
Co 2c	0	1.09	0.15	1.24	This work
		1.44	0.14	1.58	[8]
	1	1.17	0.15	1.32	This work
	2	1.18	0.13	1.31	This work
	3	1.25	0.12	1.37	This work
Co 3g	0	1.57	0.03	1.60	This work
		1.37	0.10	1.47	[8]
	1	1.72	0.05	1.77	This work
	2	1.62	0.05	1.67	This work

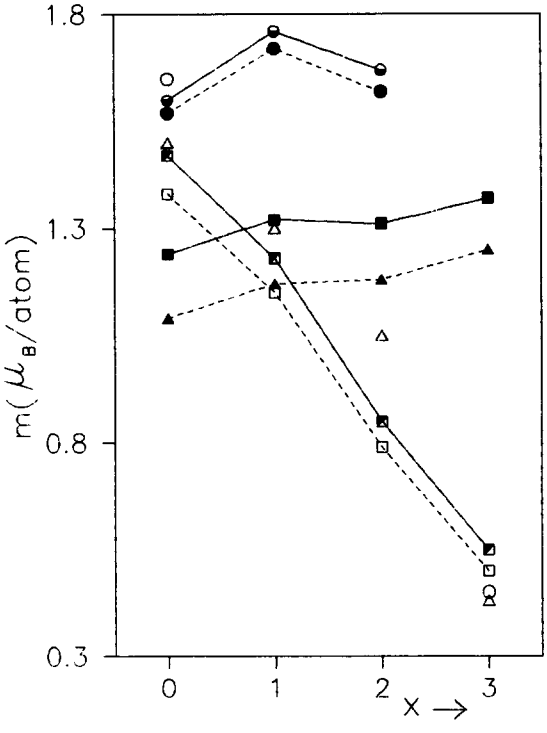

Fig. 3. The computed average (spin □, total ◩), Co 2c (spin ▲, total ■) and Co 3g (spin ●, total ◒), magnetic moments for $YCo_{5-x}Ni_x$. The experimental average magnetic moments are from [21] (○) and [22] (△).

and Poldy [13] from X-ray diffraction experiments. The YCo_5 compound often deviates to the $Y_{1-s}Co_{5+2s}$ compound, with a crystalline structure slightly different

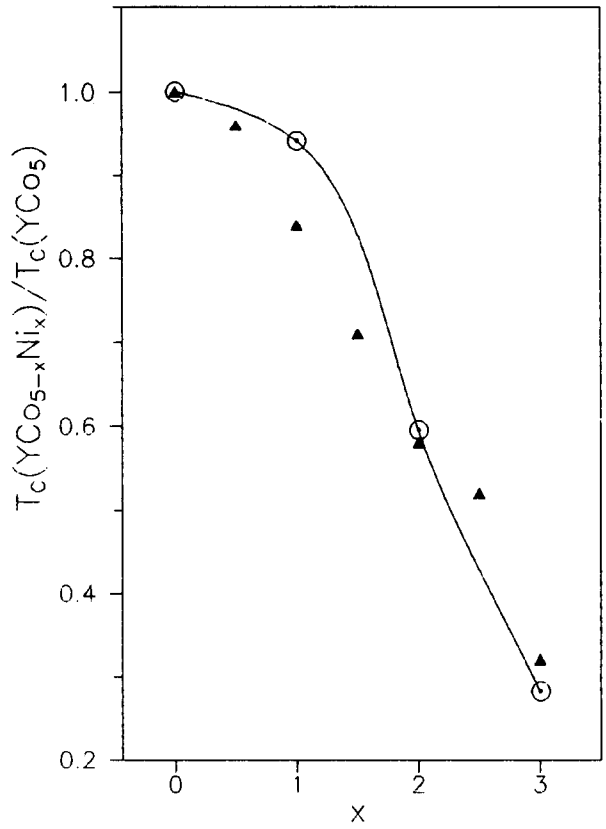

Fig 4. The ratio of the transition temperature of $YCo_{5-x}Ni_x$ and the transition temperature of YCo_5 as a function of the Ni concentration (⊙ and connected continuous line). The experimental results are from [23] (▲).

from the ideal $CaCu_5$ hexagonal structure, and with the Co atoms located in four non-equivalent sites [13].

The YNi_5 compound, the other end of this series, crystallizes in the same hexagonal $CaCu_5$ structure but the structure defects are also present [14]. This time the defects consist of random atomic substitutions of an Ni atom from the $z=0$ plane by a Y atom. In order to keep the hexagonal structure in the defect zone, the Y atoms have to maintain their Ni surroundings, so three extra Ni atoms are introduced in the $z=1/2$ plane, leading to strictions and atom displacements. The lattice parameters for YNi_5 considered in our calculation are $a=4.885$ Å and $c=3.962$ Å [13].

In our calculations, the intermetallic compounds $YCo_{5-x}Ni_x$ were considered with ideal $CaCu_5$ structure with lattice parameters varying linearly with x from those of YCo_5 to those of YNi_5. It was proved that the Ni and Co atoms are not uniformly distributed among the 2c and 3g sites; the Co atom occupies predominantly the 3g sites and the Ni atoms the 2c sites [15]. This is indicated also [16] by the non-linear dependence on concentration of the lattice parameters a and c in the system considered. Pirogov *et al.* [17] show that for $x=1$ the probability of filling the 2c sites with Ni atoms is only 0.31 and only for higher Ni

concentrations does the 2c occupation increase. In our work we considered that the Ni atoms are located only in 3g positions for all x values. The potential parameters for the elemental metals and YCo_5 compound are shown in Table 1. The actual parameters for $x=1$, 2 and 3 were computed using Andersen's formula [7] from the elemental metal parameters. As is seen from Table 1, the Y bands in our calculations are narrower and closer to the Co bands than those obtained by Nordström *et al.* [8]. In the $YCo_{5-x}Ni_x$ compounds the Wigner–Seitz radii of the Y atoms decrease as x increases because the bulk modulus of the Ni atoms is different from that of the Co atoms. So the Y states are more delocalized for the $x=5$ compound than for the $x=0$ compound.

The DOSs for $x=0$, 1, 2, 3 and 5 are shown in Fig. 1. The total and local DOSs are similar to those obtained for $La(CoNi)_5$ [18]. It is seen that DOSs for $x=1$ are very much affected by the Ni substitution. A further increase in Ni concentration resulted only in an increase of the Ni band features which were already present in the $x=1$ compound. As x increases, the low DOS region between transition metal bands and rare earth bands grows. The Sommerfeld specific heat coefficient γ, computed for the ordered phase which for $x=0$ is 30.39 mJ mol^{-1} K^{-2} decreases to 30.23 mJ mol^{-1} K^{-2} for $x=1$ but increases to 31.58 mJ mol^{-1} K^{-2} for $x=2$ and further to 33.26 mJ mol^{-1} K^{-2} for $x=3$.

The starting electronic configurations for atoms involved in calculations were Y $4d^1$, Co $3d^7$ and Ni $3d^8$. The d orbital occupation numbers are shown in Fig. 2 as a function of x. The Co d occupation numbers decrease as the Ni concentration increases, but more rapidly for 2c atoms than for 3g atoms in spite of the fact that the Ni substitution take place in the 3g sites.

In a spin-polarized neutron diffraction experiment [3] and inelastic spin-flipped neutron scattering [19], it was found that the orbital magnetic moments are very large for Co atoms ($0.46\mu_B$ per atom for 2c sites and $0.28\mu_B$ per atom for 3g sites [3]; or $0.26\mu_B$ per atom for 2c sites and $0.24\mu_B$ per atom for 3g sites [19]). Spin-polarized band structure calculations resulted in smaller values $0.14\mu_B$ per atom for 2c sites and $0.10\mu_B$ per atom for 3g sites [8] or $0.17\mu_B$ per atom for 2c sites and $0.04\mu_B$ per atom for 3g [12] sites for the orbital moments. In our calculations (with the spin-orbit interaction parameter ξ used as adjustable parameter), the resulting orbital moments for the 2c sites are larger than those for the 3g sites for all the x values, which is in good agreement with the experimental data [19]. There are no significant modifications of orbital moments with the Ni content but a very slight decrease for 2c sites and a very small increase for 3g sites (Table 2).

The mean magnetic moment on Co/Ni atoms and the magnetic moment for the Co 2c and 3g positions as a function of x, shown in Fig. 3, are in agreement with the experimental data [3]. The spin moments for the Co 3g atoms are larger than those for the Co 2c atoms.

The ratio of transition temperatures $T_c(YCo_{5-x}Ni_x)/T_c(YCo_5)$, shown in Fig. 4, decreases with x in rather good agreement with the experiment [23].

Our calculations show that, from the magnetic point of view, a periodic crystalline structure can describe rather well the properties of $YCo_{5-x}Ni_x$ compounds. The orbital moments of the Co atoms are not affected by the Ni 3g substitutions, which supports the conclusion that the Ni substitutions take place gradually in both Co sites.

References

[1] J.M. Alameda, D. Givord, R. Lemaire and Q. Lu, *J. Appl. Phys., 52* (1981) 2079.
[2] R.L. Streever, *Phys. Rev. B, 19* (1979) 2704.
[3] J. Schweizer and F. Tasset, *J. Phys. F, 10* (1980) 2799.
[4] G.H.O. Daalderop, P.J. Kelly and M.F.H. Schuurmans, *J. Magn. Magn. Mater., 104–107* (1992) 737.
[5] B. Barbara, D. Gignoux, D. Givord, F. Givord and R. Lemaire, *Int. J. Magn., 4* (1973) 77.
[6] D.G. Pettifor, *J. Phys. F, 7* (1977) 613.
[7] O.K. Andersen, O. Jepsen and M. Sob, Linear band structure methods. In M. Yussuff (ed.), *Electronic Structure and its Applications,* Springer Lecture Notes, Springer, Berlin, 1987.
[8] L. Nordström, O. Eriksson, M.S.S. Brooks and B. Johansson, *Phys. Rev. B, 41* (1990) 911.
[9] P. Mohn and E.P. Wohlfarth, *J. Phys. F, 16* (1987) 2421.
[10] B. Szpunar and W.E. Wallace, *Phys. Rev. B, 36* (1987) 3782.
[11] B. Szpunar, *Phys. Lett., 115A* (1986) 157.
[12] B. Szpunar, *J. Less-Common. Met., 127* (1987) 55.
[13] K.N.R. Taylor and C.A. Poldy, *J. Less-Common Met., 27* (1972) 255.
[14] D. Gignoux, D. Givord, R. Lemaire and A. Nait Saada, *J. Magn. Magn. Mater., 23* (1981) 274.
[15] A.N. Pirogov, A.S. Ermolenko, V.N. Dvinyaninov, V.V. Chuev and V.V. Kelarev, *Fiz. Met. Metalloved., 49* (1980) 585.
[16] J. Leforest and J.S. Shah, *IEEE Trans. Magn., 9* (1973) 217.
[17] A.N. Pirogov, V.V. Kelarev, A.S. Ermolenco, V.V. Chuev, S.K. Sidorov and A.M. Artamonova, *Sov. Phys. JETP, 56* (1982) 8804.
[18] V. Crisan, V. Popescu, A. Vernes, D. Andreica, I. Burda, S. Cristea and V. Caciuc, *J. Alloys Comp., 223* (1995) 70.
[19] A. Heidemann, D. Richter and K.H.J. Buschow, *J. Phys. B, 22* (1975) 367.
[20] R. Lemaire, *Cobalt, 33* (1966) 201.
[21] H. Oesterreicher, F.T. Parker and M. Misroch, *Solid State Commun., 19* (1976) 539.
[22] A.S. Ermolenko, A.V. Korolyov and A.F. Rojda, *IEEE Trans. Magn., 5* (1977) 1339.
[23] A.S. Ermolenko and A.F. Rojda, *Fiz. Met. Metaloved., 43* (1977) 312.