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Magnetic properties of $LaCo_{5-x}Ni_x$

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Abstract

The densities of states for $LaCo_{5-x}Ni_x$ substitutional compounds were computed using the Haydock recursion method in a self-consistent procedure. The local magnetic moments were calculated for Co sites for which the Stoner criterion for ferromagnetism was found to be fulfilled. The decrease in magnetic moments with increasing Ni concentration is explained by the changes induced in the density of states by the added Ni atoms and the decrease in exchange splitting. The transition temperatures were computed in the framework of the spin fluctuation theory, the Stoner parameter decreasing with an increase in Ni concentration.

Keywords: Magnetic properties; Nickel; Cobalt

1. Introduction

Practically almost all rare earth elements can, together with Co atoms, form a $CaCu_5$ structure. This class of compounds is important mainly because of their favorable properties for technological application as permanent magnets [1].

The $LaCo_5$ and YCo_5 compounds are especially important because the Co sublattice is also present in the permanent magnet $SmCo_5$ and the properties originating from the Co sublattice in $SmCo_5$ are common to these compounds. It was shown that an outstanding bulk low temperature magnetic hardness can be achieved solely on the basis of the Co atoms in compounds such as $YCo_{5-x}Ni_x$ and $LaCo_{5-x}Ni_x$ [2]. Compounds of this type form a complete set of solid solutions. No indication for substitution of the rare earth on the 1a site by the transition metal is found in X-ray diffraction patterns [2]. A neutron diffraction study on $ThCo_{5-x}Ni_x$ revealed a slight preference for Ni to occupy the 3g sites [3].

The magnetic properties of $LaCo_{5-x}Ni_x$ are explained on the basis of micromagnetism [2,4,5]. It was shown [6] that the transition temperature T_C and magnetic moment as functions of Ni concentration can be explained in terms of the rigid band model.

The main purpose of the present report is to compute the electronic structure and the magnetic properties of $LaCo_{5-x}Ni_x$ compounds. Details of the method are given in Section 2 and the density of states (DOS), d occupation number and magnetic properties are discussed and compared with experiment in Section 3.

2. The computational method

The DOS was computed using the recursion method of Haydock [7,8] with a tight-binding hamiltonian:

$$H=\sum_{i,j}\sum_{\mu,\nu}|i,\ \mu>t_{ij}^{\mu\nu}<\nu,\ j|+\sum_{i}\sum_{\nu}|i,\ \nu>\epsilon_i<\nu,\ i| \qquad (1)$$

where $t_{ij}^{\mu\nu}$ is the transfer integral between the orbitals μ and ν located on i and j sites respectively, and ϵ_i is the self-energy of the ith atom.

The transfer integrals are expressed in terms of the two-center hopping integrals:

$$(l_i l_j m)=N_{l_i l_j m}\left(\frac{\sqrt{S_i S_j}}{R_{ij}}\right)^{(l_i+l_j+1)}\sqrt{\Delta_{l_i}\Delta_{l_j}} \qquad (2)$$

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 and Δ_{l_i} is the width of the l_i band [9]. For two different types of atom, the Shiba approximation [10] was used. The potential parameters of the linear methods in the non-linear extrapolation scheme [11] were used as the parameters for this method. The relations between the potential parameters of the elemental atoms in pure metals and in the compound are

$$\Delta=\Delta^0\left(\frac{S}{S^0}\right)^{\mathrm{d}(\ln\Delta)/\mathrm{d}(\ln S)} \qquad (3)$$

for the band width, and

$$C=C^0+\delta(\ln S)\frac{\mathrm{d}C}{\mathrm{d}\ln S} \qquad (4)$$

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for the band's center, where the superscript 0 refers to the atoms in pure metal [12]. In this way, the parameterization problem is reduced to that of finding the Wigner–Seitz radii of the atoms in compounds. Assuming a linear dependence on pressure of the atomic volumes [11], for a binary compound we have

$$\frac{(V_A - V_A^0)/V_A^0}{(V_B - V_B^0)/V_B^0} = \frac{B_B^0}{B_A^0} \quad (5)$$

where $B_{A,B}^0$ is the bulk modulus of the elemental metal. The other condition used is either the Vegard law, when the compound obeys it, or an empirical ratio of radii of the A and B atoms deduced from the maximum filling of unit cell with Wigner–Seitz spheres.

The band width was held constant during the computation but the C parameter was determined in a self-consistent procedure with the condition of local charge neutrality.

For the magnetic moment calculations, a rigid splitting of the spin-up and spin-down bands was used [13]:

$$\Delta\epsilon = \epsilon_F^+ - \epsilon_F^- = 2\mu_B \alpha \bar{m} \quad (6)$$

where $\bar{m}$ is the mean magnetic moment and α is the molecular field coefficient. In compounds, this coefficient was used as an adjustable parameter and it was chosen to obtain $\bar{m}$ in agreement with experiment. The transition temperature was computed as in the spin fluctuation theory of Mohn and Wohlfarth [14]:

$$T_C \sim \bar{m}^2 \left(\frac{1}{2N(\epsilon_F^+)} + \frac{1}{2N(\epsilon_F^-)} - I \right) \quad (7)$$

where I is the Stoner parameter, used again as an adjustable parameter. As was already shown [15], the formula (7) gives only the trend of the compositional variation of the transition temperature, so we computed the ratio between the transition temperature of the current compound and that of the $LaCo_5$ compound.

The Stoner product in the multiband version [16, 17] is given by

$$IN(\epsilon_F) = N(\epsilon_F) \sum_{qll'} \frac{N(\epsilon_F)_{ql}}{N(\epsilon_F)} I_{qll'} \frac{N(\epsilon_F)_{ql'}}{N(\epsilon_F)} \quad (8)$$

where $N(\epsilon_F)$ and $N(\epsilon_F)_{ql}$ are the total and projected DOS for site q and angular momentum l at the Fermi level ϵ_F and $I_{qll'}$ are the intra-atomic exchange integrals. The local Stoner product is

$$(IN(\epsilon_F))_{local} = N(\epsilon_F)_q \sum_{ll'} \frac{N(\epsilon_F)_{ql}}{N(\epsilon_F)_q} I_{qll'} \frac{N(\epsilon_F)_{ql'}}{N(\epsilon_F)_q} \quad (9)$$

where $N(\epsilon_F)_q$ is the site projected DOS at ϵ_F.

3. Results and discussions

The $LaCo_5$ and $LaNi_5$ compounds have a $CaCu_5$-type structure with space group $P6/mmm$. One important property of this type of structure is the existence of two inequivalent structural Cu sites: 3g with the point group mmm and 2c with the point group $6\bar{m}2$. In the $LaCo_{5-x}Ni_x$ compounds we considered that the Ni atoms substitute gradually for the Co atoms from the 3g positions.

The lattice parameters a and c were taken as 9.61 and 7.45 a.u. for $LaCo_5$, 9.48 and 7.53 a.u. for $LaNi_5$ and, for the $LaCo_{5-x}Ni_x$ compounds a linear dependence on concentration x was considered. The potential parameters used in the present calculations for $LaCo_5$ are listed in Table 1 together with the values used by Nordström et al. [18]. It is obvious that the band width

Table 1
The potential parameters for elemental metals (first line) and for the $LaCo_5$ compound, S denotes the Wigner–Seitz radius, C the band center (self-energy) and Δ the band width

S_{La} (Å)	S_{Co} (Å)	C_{La} (Ry)	C_{Co} (Ry)	Δ_{La} (Ry)	Δ_{Co} (Ry)	Reference
2.1077	1.36	0.046	−0.123	0.029	0.015	[12]
2.050	1.356	0.0831	−0.1177	0.032	0.0152	This work
1.870	1.428	0.1916	−0.1995	0.116	0.0849	[18]

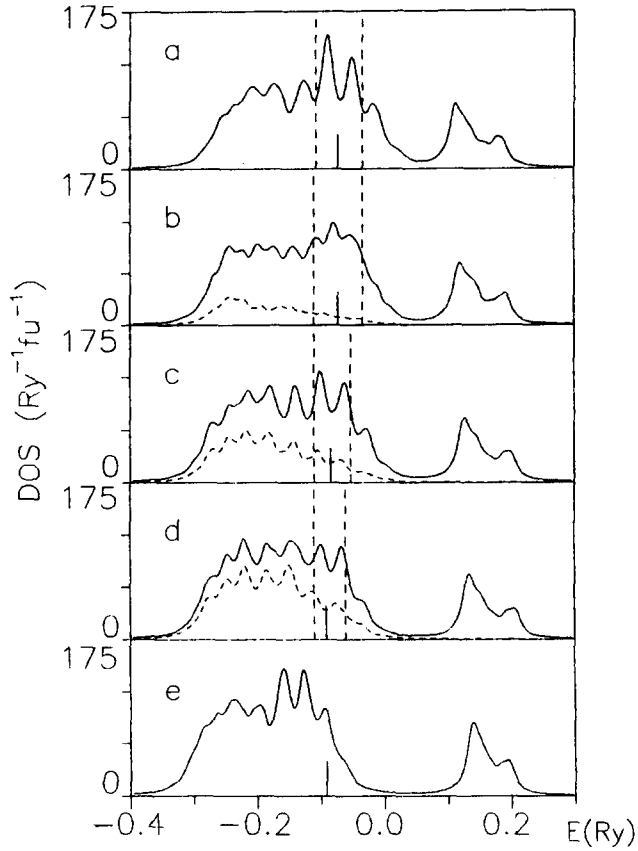

Fig. 1. The total DOS for $LaCo_{5-x}Ni_x$ with $x=0$ (a), $x=1$ (b), $x=2$ (c), $x=3$ (d) and $x=5$ (e). The dashed curves show the Ni contribution to the total DOS. The short vertical line marks the paramagnetic Fermi level and the vertical dashed lines mark the Fermi levels for the minority and majority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

of both the La and Co atoms in the $LaCo_5$ increases with smaller values with respect to the band width in elemental metals.

The DOSs obtained for different x values are shown in Fig. 1. We noticed that the $LaCo_5$ and $LaNi_5$ compounds have almost the same DOS, which could provide support for a rigid band model. However, it is seen from Fig. 1(b,c,d) that this assumption is not appropriate because the shape of the DOS is changed greatly as a function of x.

The electronic configuration of the atoms used as input in DOS calculations was $5d^1$, $3d^7$ and $3d^8$ for La, Co and Ni respectively. In compounds, the d-electron occupation number for La atoms increases up to 1.53 (in agreement with the results of Nordström et al. [18] but in disagreement with Oesterreicher et al. [2]) at the expense of the Co atom d-electrons. When the Co atoms were substituted by Ni atoms the d-electron occupation number for La and Co decreased with Ni concentration (Fig. 2). According to our expectations, owing to their electronegativity, the Ni atoms attract the electrons belonging to the neighboring atoms especially when the Ni concentration is small.

It was proved by experiment [3] that for $x \leqslant 2$ the decrease in magnetic moments obeys a linear law. At higher Ni concentrations, the magnetic moments start to decrease much faster than predicted by the rigid band picture [19], and it was believed that the substitution of Co atoms by Ni atoms not only adds one electron to the Co d bands but also affects the magnetic splitting between them. The magnetic band splitting must collapse somewhere between $LaCo_5$ and $LaNi_5$ because the latter compound is a Pauli paramagnet.

The obtained DOS curves for x varying from 0 to 3 show that not only was the magnetic splitting between the 3d bands affected, but the shape of the DOSs themselves were changed.

The calculated mean magnetic moment on Co/Ni atom seems to be in agreement with the experimental data [5,20].

In spite of the considerable height of the DOS at the Fermi level in all the compounds, only the Co atoms have the local Stoner product greater than unity, i.e. the Stoner criterion for ferromagnetism is fulfilled only for these atoms (Table 2).

The calculated local magnetic moments are larger for 3g positions (Fig. 3). The results do not match with

Table 2
The local Stoner product $(IN)_{local}$ in $LaCo_{5-x}Ni_x$ for 2c and 3g (g1, g2, g3) sites

x	$(IN)_{local}$			
	2c	g1	g2	g3
0	1.07	1.72	1.72	1.72
1	1.95	0.88	2.53	2.53
2	1.18	0.92	0.92	2.22
3	2.11	0.91	0.91	0.91

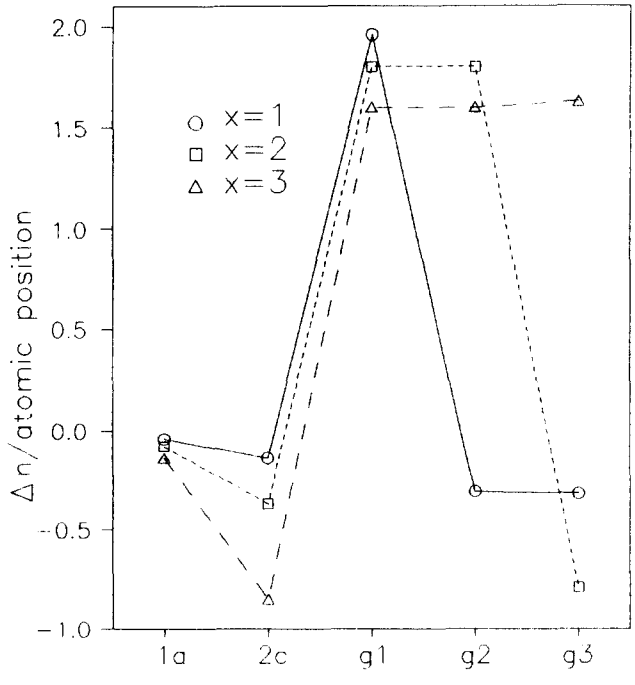

Fig. 2. The d-electron occupation number variation Δn for $LaCo_{5-x}Ni_x$ with respect to the $LaCo_5$ compound on different atomic positions 1a, 2c, 3g (g1, g2, g3).

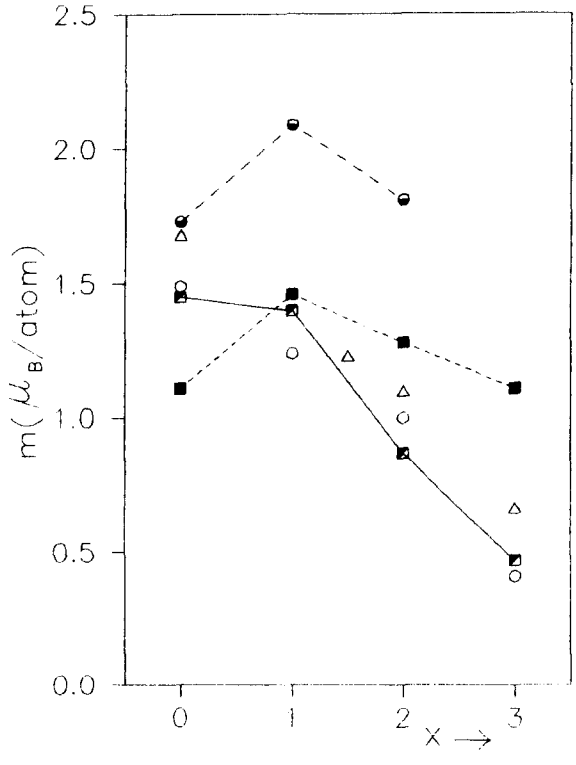

Fig. 3. The calculated mean magnetic moment (◩), and the Co 3g (◒) and Co 2c (■) local magnetic moments for $LaCo_{5-x}Ni_x$. The experimental values are from [20] (△) and [5] (○).

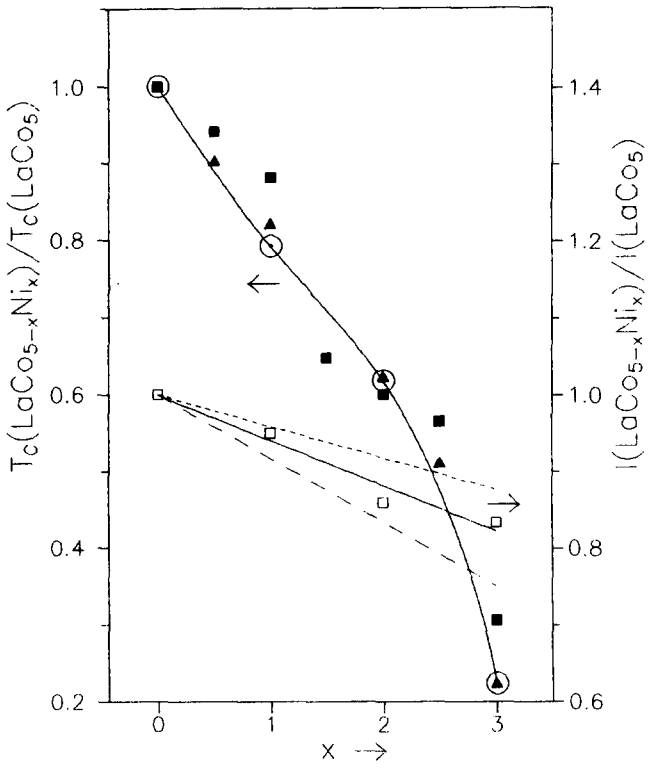

Fig. 4. The ratio of the transition temperature of $LaCo_{5-x}Ni_x$ and the transition temperature of $LaCo_5$ as a function of Ni concentration (⊙ and connected continuous line). The experimental results are from [20] (■) and [5] (▲). The ratio of the Stoner parameters of $LaCo_{5-x}Ni_x$ and Stoner parameter of $LaCo_5$ as a function of x (□ and connected continuous line) is also shown.

those of Nordström et al. [18] who obtained magnetic moments for 2c sites larger than those for 3g sites. As much as we know, neutron diffraction experiments are not yet available for $LaCo_5$, but in the isostructural compound YCo_5 the Co 3g moments were found to be larger than those for Co 2c [21].

The transition temperature ratios computed for different Ni concentrations are in agreement with the experimental data when the Stoner effective interaction parameter has a linear variation, as shown in Fig. 4. It is seen that the Stoner parameter ranges between the strongly correlated and uncorrelated system limits (computed using rigid band model [3]).

The results obtained show good agreement with the experimental data for both the transition temperature and local and total magnetic moments, which could be an argument for the homogeneity of the Ni distribution on the 3g positions. This would suggest that the effective domain wall pinning centers are not related to the crystallographic disorder on transition metal sites, at least for low concentrations of Ni atoms.

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