Title: Ab initio study of electronic structure and magnetic properties of Gd(Ni 1-xFex)3 alloys

Author: Józef Deniszczyk, Andrzej Woźniakowski, Władysław Borgieł

Citation style: Deniszczyk Józef, Woźniakowski Andrzej, Borgieł Władysław. (2012). Ab initio study of electronic structure and magnetic properties of Gd(Ni 1-xFex)3 alloys. "Acta Physica Polonica A" (Vol. 121, nr 5/6 (2012), s. 1156-1158).

UNIWERSYTET ŚLĄSKI W KATOWICACH   Biblioteka Uniwersytetu Śląskiego   Ministerstwo Nauki i Szkolnictwa Wyższego

Ab Initio Study of Electronic Structure and Magnetic Properties of Gd(Ni₁₋ₓFeₓ)₃ Alloys

J. Deniszczyk*, A. Woźniakowski

Institute of Materials Science, University of Silesia, Bankowa 12, 40-007 Katowice, Poland

and W. Borgieł

August Chełkowski Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

We present the *ab initio* investigations of the electronic and magnetic properties of magnetocaloric Gd(Ni₁₋ₓFeₓ)₃ alloys. To simulate fractional concentrations the supercell approach was implemented and different configurations of iron atoms were considered. Energetical analysis of site preference and magnetic order was performed. The concentration dependence of the averaged total and local magnetic moments and of the valence band photoemission spectra are presented and discussed in reference to experimental data.

PACS: 71.20.Be, 79.60.Bm

1. Introduction

Metallic gadolinium serves as a generic material for a magnetocaloric application but due to high costs and high chemical reactivity in a pure form cannot be used. A transition-metal (TM) alloys with gadolinium are extensively studied in searching for a new magnetocaloric materials. Recently the electronic structure and magnetic properties of crystalline Gd(Ni₁₋ₓFeₓ)₃ alloys were measured by means of different methods [1]. The measurements have shown that in the Ni-rich region the alloys display magnetocaloric properties but with relatively low Curie temperature. Increasing the Fe contents yields a linear decrease of the saturation magnetization while the Curie temperature reaches the maximum at $x \approx 0.5$. The X-ray photoelectron spectroscopy (XPS) valence band measurements reveal the presence of correlation between the magnetic properties and electronic structure near the Fermi level. In addition, the shift of Gd $4f$ band to lower binding energy (BE) and broadening with increasing iron contents was observed. The aim of presented investigations was to determine the electronic structure, structural and magnetic properties of Gd(Ni₁₋ₓFeₓ)₃ alloys by the *ab initio* methods and elucidate the microscopic origin of observed properties.

2. Computational procedure

The electronic structure calculations were performed using the WIEN2k code [2] based on the full-potential linearized augmented plane wave (FP-LAPW) method [3]. The electronic states were partitioned into core states: ([Kr]$4d^{10}$ for Gd and [Ne] for Fe and Ni); local orbitals

---

* corresponding author; e-mail: `jozef.deniszczyk@us.edu.pl`

[3] ($5s$, $5p$ for Gd and $3s$, $3p$ for Fe and Ni) and valence states ($4f$, $5d$, $6s$ for Gd and $3d$, $4s$ for Ni and Fe). The core states were treated in a fully relativistic manner while for the local orbitals and valence states the scalar-relativistic approximation was applied. The GGA exchange-correlation (XC) potential was used in the form given in [4]. For the strongly correlated Gd $4f$ band states the XC potential was corrected by the Hubbard correlation interaction using the GGA+U method [5]. The effective $U_{\mathrm{eff}} = 0.55$ Ry was established by fixing the majority spin Gd $4f$ band at their BE measured in GdNi₃ and was kept fixed for all calculated compositions. Atomic muffin-tin spheres radii were taken as 2.5 a.u. and 2.3 a.u. for Gd and Fe(Ni), respectively. The $\boldsymbol{k}$-mesh was generated such as to provide approximately 200 $\boldsymbol{k}$ points in the irreducible wedge of the Brillouin zone. Other parameters influencing the computational precision [2] were fixed to assure the total energy precision of 10^{-1} mRy. The XPS spectra were calculated by convolution of partial densities of states (DOS) with Lorentzians of 0.25 eV width and multiplication by corresponding cross-sections [6].

3. Results and discussion

In the whole concentration range Gd(Ni₁₋ₓFeₓ)₃ alloys crystallize in the rhombohedral crystal structure of PuNi₃-type (space group No. 166). The primitive cell consists of three formula units. Gd atoms occupy single 3a $(0, 0, 0)$ and double 6c $(0, 0, z_1)$ positions. The TM (Ni, Fe) atoms locate at single-3b $(0, 0, 1/2)$, double-6c $(0, 0, z_2)$ and sixfold-18h $(x, -x, z_3)$ sites. We have optimized the structure of parent GdNi₃ compound with respect to volume and c/a ratio and then internal atomic coordinates were relaxed. The optimized volume and lattice parameters of GdNi₃ differ from the experimental

values by less than 0.5%. Relaxation of atomic positions for GdNi$_3$ gave $z_1 = 0.1393$, $z_2 = 0.3329$, $z_3 = 0.0813$ and $x = 0.5005$. Calculations were performed for the whole iron concentration range with the step $\Delta x_{Fe} = \frac{1}{9}$. The lattice parameters were taken from the interpolation of experimental data [1]. The relaxed internal coordinates obtained for GdNi$_3$ were applied for all studied compositions. In simulations of fractional concentration, for each concentration several configurations of iron atoms would have to be considered. Due to symmetry the number of possible iron configurations can be reduced significantly, e.g. for $n_{Fe} = 1$ ($x_{Fe} = 0.11$) only three nonequivalent configurations exist: Fe in 3b, Fe in 6c and Fe in 18h site. For concentration $x_{Fe} = 0.11$ we have performed detailed energy analysis of site-preference and magnetic order, assuming parallel (FM) and antiparallel (AF) alignment of iron magnetic moments with respect to that of gadolinium.

The results are collected in Table where the lowest total energy of the AF solution with single iron at 18h was taken as the reference energy. We have found the preference of iron atoms to locate at 6c or 18h sites. For all configurations the AF magnetic order is energetically preferable, but the energy distance between AF and FM solutions for Gd(Ni$_{0.89}$Fe$_{0.11}$)$_3$ is of only ≈ 20 meV/atom (≈ 230 K) which compares with $k_B T_C$ for this alloy [1]. The difference between the FM and AF solution calculated for GdFe$_3$ was found few times larger (≈ 90 meV/atom) and for GdNi$_3$ compound only single ferrimagnetic ground state solution has been found.

TABLE

Relative energies for site preference of iron atoms and magnetic order in Gd(Ni$_{0.89}$Fe$_{0.11}$)$_3$. The total energy of AF solution for Fe 18h configuration is used as the reference energy.

Magnetic order	ΔE [meV/atom]		
	Fe–3b	Fe–6c	Fe–18h
FM	46	17	19
AF	24	1	0

Local atomic and total magnetic moments calculated for the AF magnetic order are presented in Fig. 1. For a given concentration the total magnetic moment for different configurations vary only slightly (Fig. 1a). The experimental dependence of the saturation magnetization on iron concentration in Gd(Ni$_{1-x}$Fe$_x$)$_3$ is reproduced perfectly. We have found linear correlation $M_{tot}(n_{Fe}) \approx -1.9 n_{Fe}$. The averaged atomic moments vary only minutely with iron concentration (Fig. 1b). The μ_{Gd} moment increases linearly from $\mu_{Gd} = 7.12$ μ_B in GdNi$_3$ to $\mu_{Gd} = 7.30$ μ_B in GdFe$_3$. Magnetic moments of TM ions polarize oppositely to μ_{Gd}. Magnitude of μ_{Ni} increases from 0.23 μ_B at $x = 0.00$ to 0.59 μ_B at $x = 0.89$ while that of μ_{Fe} decreases from 2.52 μ_B at $x = 0.11$ to 2.35 μ_B at $x = 1.00$. The dependence of the averaged TM atomic moments on concentration x_{Fe} can be described

by linear relation: $\overline{\mu_{TM}} \approx -2.1 x_{Fe} - 0.32$. The calculated magnitudes of $\overline{\mu_{TM}}$ exceed those estimated on the basis of saturation magnetization measurements [1].
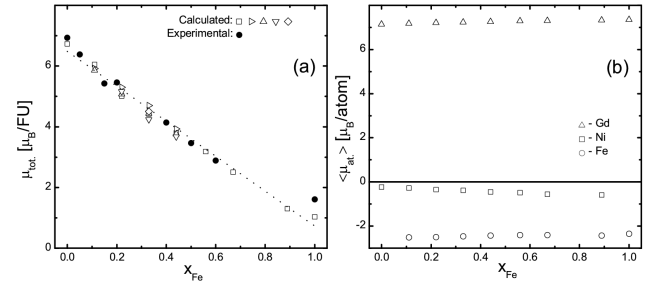

Fig. 1. Dependence of the calculated total (a) and averaged atomic (b) magnetic moments on iron concentration compared with experimental saturation moment [1]. Open symbols in (a) represent M_{tot} for different configurations of Fe atoms and dashed line shows the linear fit to the concentration dependence of average M_{tot}. Atomic magnetic moments, shown in (b) were obtained by averaging over configurations and over nonequivalent atomic positions.
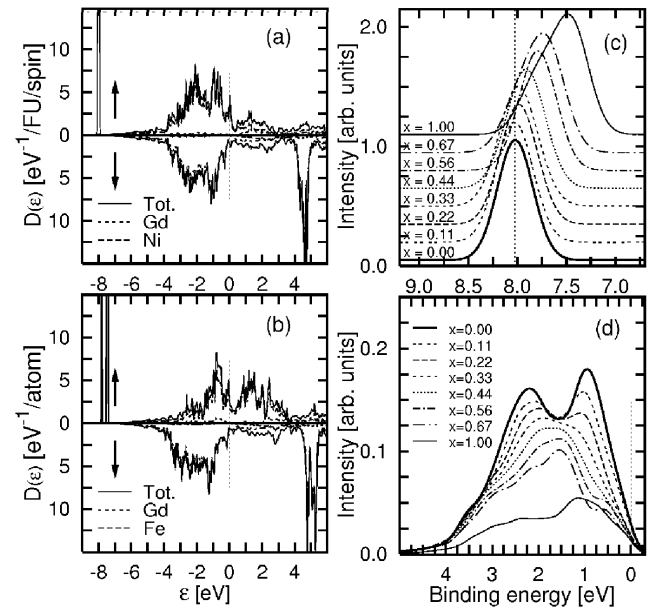

Fig. 2. Spin resolved total DOS with separated partial atomic contributions calculated for GdNi$_3$ (a) and GdFe$_3$ (b) compounds. Simulated XPS spectra for Gd(Ni$_{1-x}$Fe$_x$)$_3$ alloys — (c) and (d).

Figure 2 shows the essential results for electronic structure of Gd(Ni$_{1-x}$Fe$_x$)$_3$ alloys. For clarity, we separated simulated valence band spectra into two energy windows. The dependence of the BE of Gd $4f$ states on iron concentration reproduces quantitatively experimental data [1]. Upon complete replacement of nickel by iron the BE of Gd $4f$ states decreases by $\Delta_{BE} \approx 0.51$ eV (for comparison $\Delta_{BE}^{exp} = 0.6$ eV). Similarly as in experimental spec-

tra, the calculated $4f$ line begins to shift to lower BE at $x_{Fe} = 0.22$ and with increasing iron content the shift grows monotonically. Detailed analysis of partial density of states (DOS) has shown that BE of the Gd $4f$ orbitals strongly depends on the position occupied by Gd (3a or 6c) and on the chemical composition of the nearest neighbour (NN) sites. Gadolinium atoms at 3a ($Gd^{(3a)}$) and 6c ($Gd^{(6c)}$) sites differ in their local atomic environment. The $Gd^{(3a)}$ atom neighbors with six TM (Ni, Fe) atoms located at 6c sites ($d_{NN} = 2.88$ Å). The $Gd^{(6c)}$ has six TM neighbors at 18h sites ($d_{NN} = 2.86$ Å) and three TM atoms at NNN 3b sites ($d_{NNN} = 2.96$ Å). Calculations have shown that in $GdNi_3$ and $GdFe_3$ compounds the $Gd^{(3a)}-4f$ and $Gd^{(6c)}-4f$ are split by ≈ 0.05 eV and ≈ 0.43 eV, respectively. For a given concentration of Fe atoms in $Gd(Ni_{1-x}Fe_x)_3$ alloys the shift of the Gd $4f$ depends also on the distribution of Fe atoms among the 3a, 6b and 18h sites.

For concentrations $x_{Fe} = 0.11$, 0.22 and 0.33 we have tested different configurations of iron atoms. For $x_{Fe} = 0.11$ the Gd_{3a} and Gd_{6c} the BE of $4f$ states changes only slightly with respect to that in $GdNi_3$. For $x_{Fe} = 0.22$ the $Gd_{3a}-4f$ states either do not move or shift slightly to higher BE while $4f$ states of Gd_{6c} with four iron atoms at NN sites shift to lower BE by ≈ 0.11 eV. For $x_{Fe} = 0.33$ the iron atoms at 18h sites do not change the BE of $Gd_{3a}-4f$ states, while when iron atoms occupy completely the 3b and 6c sites they yield the shift of $Gd_{3a}-4f$ states to higher BE by ≈ 0.16 eV. For the Gd_{6c} atoms we have found that when up to two iron atoms locate at NN sites the BE of $4f$ states changes only minutely while the presence of four and six iron atoms at NN sites of Gd_{6c} atom gives the shift of BE by ≈ 0.12 eV and ≈ 0.53 eV, respectively. It is worth to note that the Gd $4f$ states of majority and minority spin shift rigidly, leaving the exchange splitting constant. For higher iron concentration the $Gd_{3a}-4f$ states gradually shift to lower BE while the reduction of BE of $Gd_{6c}-4f$ states is more significant. Because the shift to lower BE of $4f$ states in Gd_{3a} and Gd_{6c} atoms is different, the splitting of the both group of states grows with increasing iron content. This calculated property explains the broadening of $4f$ line with increasing iron concentration observed on measured XPS spectra [1]. We tried to analyse the shift of $4f$ states in terms of the *chemical shift* model, relating the changes of BE of outer atomic orbitals to the changes in the screaning of ionic potential caused by electronic transfer between atoms in unit cell. We did not find correlation between the shift of $4f$ BE and interatomic electronic transfer. Calculated changes

of the charge density inside Gd-nucleus, which might indicate intraatomic electronic charge redistribution, also do not correlate with shifts of Gd $4f$ states.

In the $Gd(Ni_{1-x}Fe_x)_3$ alloys with AF magnetic order, the minority spin $3d$ bands of TM atoms do not change qualitatively upon alloying (Fig. 2a, b). They are almost completely occupied, and keep below the Fermi level. The majority spin Fe $3d$ states locate around the Fermi level, far above the Ni $3d$ states. With increasing iron content the DOS around the Fermi level enhances at the expense of the DOS at BE > 2 eV. This redistribution of majority spin $3d$-states affects the valence band photoemission spectra visible in Fig. 2d. In this respect the calculated XPS agrees qualitatively with the results of measurements [1].

4. Summary

The electronic structure calculations for $Gd(Ni_{1-x}Fe_x)_3$ series have shown the energetical preference for antiparallel mutual alignment of Gd and TM local magnetic moments. The calculated dependences of saturation magnetization and valence band photoemission spectra on iron concentration reproduce quantitatively the measured ones.

Acknowledgments

References

[1] A. Bajorek, A. Chrobak, G. Chełkowska, M. Kwiecień, *J. Alloys Comp.* **485**, 6 (2009).

[2] *Electronic structure calculations of solids using the WIEN2k package for material science*, K. Schwarz, P. Blaha, G.K.H. Madsen, *Comp. Phys. Commun.* **147**, 71 (2002).

[3] D. Singh, *Plane Waves, Pseudopotentials and the LAPW Method*, Kluwer Academic, Boston 1994.

[4] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[5] V.I. Anisimov, F. Aryasetiawan, A.I. Lichtenstein, *J. Phys., Condens. Matter* **9**, 767 (1997).

[6] J.J. Yeh, I. Lindau, *At. Data Nucl. Data Tables* **32**, 1 (1985).