Ab Initio Study of Electronic Structure and Magnetic Properties of Gd(Ni$_{1-x}$Fe$_x$)$_3$ Alloys

J. DENISZCZYK*, A. WOŹNIAKOWSKI
Institute of Materials Science, University of Silesia, Bankowa 12, 40-007 Katowice, Poland
AND W. BORGIEL
August Chelkowski 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(Ni$_{1-x}$Fe$_x$)$_3$ 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.

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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(Ni$_{1-x}$Fe$_x$)$_3$ 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(Ni$_{1-x}$Fe$_x$)$_3$ 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 [Ar] for Fe and Ni; local orbitals

\[ 3 \] (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 $U_{eff} = 0.55$ Ry was established by fixing the majority spin Gd 4f band at their BE measured in GdNi$_3$ 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 \( k \)-mesh was generated such as to provide approximately 200 \( k \) 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(Ni$_{1-x}$Fe$_x$)$_3$ alloys crystallize in the rhombohedral crystal structure of PuNi$_3$-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 GdNi$_3$ compound with respect to volume and $c/a$ ratio and then internal atomic coordinates were relaxed. The optimized volume and lattice parameters of GdNi$_3$ differ from the experimental

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

(1156)
values by less than 0.5%. Relaxation of atomic positions for GdNi3 gave $z_1 = 1.383$, $z_2 = 0.3329$, $z_3 = 0.0813$ 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 GdNi3 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(Ni0.80Fe0.11)3 is of only $\approx 20$ meV/atom ($\approx 230$ K) which compares with $\delta T_C$ for this alloy [1]. The difference between the FM and AF solution calculated for GdFe3 was found few times larger ($\approx 90$ meV/atom) and for GdNi3 compound only single ferrimagnetic ground state solution has been found.

<table>
<thead>
<tr>
<th>Magnetic order</th>
<th>$\Delta E$ [meV/atom]</th>
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<tr>
<td></td>
<td>Fe–3b</td>
</tr>
<tr>
<td>FM</td>
<td>46</td>
</tr>
<tr>
<td>AF</td>
<td>24</td>
</tr>
</tbody>
</table>

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(Ni1-xFe3)x3 is reproduced perfectly. We have found linear correlation $M_{sat}(n_{Fe}) = -1.9n_{Fe}$. The averaged atomic moments vary only minutely with iron concentration (Fig. 1b). The $\mu_{Gd}$ moment increases linearly from $\mu_{Gd} = 7.12 \mu_B$ in GdNi3 to $\mu_{Gd} = 7.30 \mu_B$ in GdFe3. Magnetic moments of TM ions polarize oppositely to $\mu_{Gd}$. Magnitude of $\mu_{Ni}$ increases from $0.23 \mu_B$ at $x = 0.00$ to $0.39 \mu_B$ at $x = 0.89$ while that of $\mu_{Fe}$ decreases from $2.52 \mu_B$ at $x = 0.11$ to $2.35 \mu_B$ at $x = 1.00$. The dependence of the averaged TM atomic moments on concentration $x_{Fe}$ can be described by linear relation: $\mu_{TM} \approx -2.1x_{Fe} - 0.32$. The calculated magnitudes of $\mu_{TM}$ exceed those estimated on the basis of saturation magnetization measurements [1].

Figure 2 shows the essential results for electronic structure of Gd(Ni1-xFe3)x3 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 $\Delta_{BE} = 0.6$ eV). Similarly as in experimental spec-
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 ($d_{NN} = 2.88 \text{ Å}$). The Gd(6c) has six TM neighbors at 18t sites ($d_{NN} = 2.86 \text{ Å}$) and three TM atoms at NNN 3b sites ($d_{NNN} = 2.96 \text{ Å}$). Calculations have shown that in GdNi$_3$ and GdFe$_3$ compounds the Gd(3a)-4f and Gd(6c)-4f are split by $\approx 0.05$ eV and $\approx 0.43$ 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 18t 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 $\approx 0.11$ eV. For $x_{Fe} = 0.33$ the iron atoms at 18t 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 $\approx 0.16$ 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 $\approx 0.12$ eV and $\approx 0.53$ 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 screening 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 intratantalonic 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

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References