On the nickel magnetic behaviour in rare-earths compounds

E Burzo\(^1\),\(^2\) and P Vlaic\(^3\)

\(^1\) Faculty of Physics, Babes-Bolyai University 40084 Cluj-Napoca, Romania
\(^2\) Romanian Academy, Cluj-Napoca Branch, 400015, Cluj-Napoca, Romania
\(^3\) University of Medicine and Pharmacy Iuliu Hatieganu, Biophysics Department, 400023 Cluj-Napoca, Romania

E-mail: vlaic_pc@yahoo.com

Keywords: rare-earth nickel compounds, magnetic properties, electronic structure

Abstract
The x-ray photoelectron spectroscopy (XPS) study, magnetic measurements and band structure calculations were performed on RNi\(_2\), RNi\(_3\), RNi\(_5\) and R\(_2\)Ni\(_{17}\) compounds, where R is a rare-earth or yttrium. The presence of small nickel moments was shown in almost all compounds with magnetic rare-earths. The nickel moments are dependent on the site location, their local environment, respectively. The R5d bands are negatively polarized, their values M\(_{5d}\), being determined by additive contributions resulting from local 4f-5d and short-range 5d-3d interactions. The R5d band polarizations mediate the exchange interactions within the spatial extension of the unit cell. The Curie temperatures for a given series are linearly dependent on M\(_{5d}\) values with the same rate for both heavy and light rare-earth compounds.

1. Introduction
The R-Ni phase diagrams, where R is a rare-earth or yttrium, in the composition range 66.7–88.5 at\%, show the presence of RNi\(_2\), RNi\(_3\), RNi\(_5\) and R\(_2\)Ni\(_{17}\) series [1]. The RNi\(_2\) compounds crystallize in a cubic-type structure, the RNi\(_3\) in hexagonal CaCu\(_3\)-type lattice, RNi\(_5\) in a rhombohedral structure having R\(_3m\) space group, R\(_2\)Ni\(_3\) in hexagonal P\(_\overline{6}m\) space and R\(_2\)Ni\(_5\) series crystallize in both hexagonal (P\(_\overline{6}m\)/mmc) and rhombohedral (R\(_3m\)) type structures. In cubic RNi\(_2\) Laves phases, each R and Ni atoms are located on only one type of site, while in RNi\(_3\), the R atoms occupy 1a site and Ni the 2c and 3 g positions. The number of inequivalent R and Ni sites is higher in other R-Ni compounds, two R and three Ni in RNi\(_3\) compounds and two R and four or five Ni sites in R\(_2\)Ni\(_3\) and R\(_2\)Ni\(_5\) series [1], respectively.

The R-Ni compounds have interesting physical properties as well as technical applications, as for example R\(_3\)Ni\(_3\) series, which are used for hydrogen storage [2]. The R-Ni compounds generally show collinear magnetic structures. Little canted magnetic structures were reported in RNi\(_3\) (R = Tb, Dy) [3] and Tm\(_3\)Ni\(_3\) [4] compounds. The nickel, generally has been reported to be non-magnetic in RNi\(_2\) [5], RNi\(_3\) [3] and RNi\(_5\) [6] compounds, or to have a small magnetic moment, of 0.2–0.3 \(\mu_B\)/Ni atom, in R\(_2\)Ni\(_5\) [7] and R\(_2\)Ni\(_7\) [4, 8, 9] series. When nickel has a magnetic moment, the compounds, with magnetic heavy rare-earths, are ferrimagnetically ordered, while those with light rare-earth, show parallel orientations of R and Ni moments. Later on, by means of magnetic circular dichroism study on GdNi\(_2\), has been evidenced that nickel has a magnetic moment of \(M_{Ni} \approx 0.2 \mu_B\) [10]. Information concerning the presence of nickel moment in Ni-based alloys has been obtained also by x-ray photoelectron spectroscopy (XPS) [11, 12]. The presence of 6 eV satellites in XPS core level and valence band spectra were associated with the partially filled Ni3d band which allows the creation of two hole bond state on Ni atoms after photoionization event [13, 14]. The intensities of the satellites can give information about the Ni3d hole density in nickel alloys [15, 16] or rare-earth-nickel intermetallic compounds [17–19]. Small Ni moments were determined by means of band structure calculations of RNi\(_2\) and RNi\(_3\) series with magnetic rare-earths [20].

The Curie temperatures, T\(_C\), of the RNi\(_2\), RNi\(_3\), RNi\(_5\) and R\(_2\)Ni\(_{17}\) series follow linear dependencies on the De Gennes factor, \(G = (g - 1)^2J(J + 1)\), with different rates for light and heavy rare-earths compounds [1]. No explanation of the above mentioned trend is given. The Curie temperatures are the result of complex magnetic
interactions at the level of the unit cell. The exchange interactions between rare-earths and nickel atoms are best described by the 4f-5d-3d model, being mediated by the R5d band polarizations, M5d \[20, 21\]. The M5d values, as evidenced in R-Co compounds, mirror all the changes in their magnetic properties resulting from the substitutions at R and Co sites as well as those resulting from the pressure effects \[22\].

Starting from the band structure calculations and based on the 4f-5d-3d exchange interactions model, it is our aim to analyze: (1) the presence and the values of the nickel moments and R5d band polarizations in R-Ni series, as well as their site (local environment) dependencies, respectively; (2) the reason for different rates of $T_C$ versus $G$, for a given series in the light and heavy rare-earths nickel compounds. Thus, in addition to the previous data obtained from band structure calculations on RNi5, RNi15, and RNi17 heavy rare-earth compounds \[20\], the band structures of the corresponding compounds with light rare-earths as well as of RNi3 series are now reported. The XPS study for some RNi3 compounds as well as the results of the magnetic measurements, particularly the T_C values, of some R-Ni compounds are also presented and correlated with those determined from the band structure calculations.

Starting from the computed magnetic properties as well as the experimental data, the presence of small nickel moments are evidenced in nearly all compounds with magnetic rare-earths. The R5d band polarizations mediate the exchange interactions within the spatial extension of the unit cell. Consequently, for a given series, linear dependence of T_C versus M5d is evidenced with the same rate for both heavy and light rare-earth-nickel compounds.

2. Experimental and computing methods

The x-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI5600ci multitechnique system. The spectra were recorded using the monochromatized K$_\alpha$ radiation of Al. The total energy resolution of the electron spectra, as determined at the Fermi level of gold foil, was 0.3–0.4 eV. Binding energies are given with reference to the Fermi level, EF. The spectra were recorded in vacuum below 5 · 10^{-10} mbar. The fractured samples contained only a tiny amount of oxygen and carbon.

The magnetic measurements have been performed for R$_2$Ni$_{17}$ (R = Dy and Er) and SmNi$_3$ compounds for which the previously reported Curie temperatures and magnetizations covered a large range of values \[1\]. The present data were obtained by using a VSM equipment, in the temperature range 4.2–300 K and external fields up to 7 T.

The band structure calculations were performed in the framework of density functional theory (DFT) with two different schemes. The greatest part of data (RNi5, RNi3, R$_2$Ni$_{17}$, Y$_2$Ni$_{17}$) were obtained assuming localized 4 f electrons, by using tight-binding linear muffin-tin orbital (TB-LMTO) formalism \[23—25\]. The exchange correlation energy was the free electron gas parameterization of Von Barth and Hedin \[26\]. Relativistic effects were included. Band structure calculations were also performed for RNi$_2$, RNi$_3$, and some RNi$_5$ compounds, considering the 4f electrons in the valence band, within the LSDA + U approach, respectively \[27\]. An intra-atomic Coulomb interaction parameter $U_f = 9$ eV and exchange interaction $J_f = 0.9$ eV were used for rare-earths \[27, 28\]. For nickel, the parameters $U_d = 2$ eV and $J_d = 0.9$ eV were considered \[29\]. The determined nickel moments, as well as the R5d band polarizations, obtained by the above approaches are rather close as evidenced in RNi$_2$, RNi$_3$, and RNi$_5$ series \[20\]. Only the magnetic properties of Y$_2$Ni$_7$ compound were investigated from R$_2$Ni$_7$ series.

3. Results and discussions

The Ni2p$_{3/2}$ and Ni2p$_{1/2}$ core level lines of NdNi$_3$ compound are plotted in figure 1. The decomposed spectrum is also shown. As in case of metallic nickel, the Ni2p$_{3/2}$ and Ni2p$_{1/2}$ lines are located at $\approx$852.5 eV and 869.8 eV. In the spectrum the presence of the 6 eV nickel satellite at higher binding energy is evidenced, suggesting that there are unoccupied Ni3d states. The intensities of the above satellites are smaller than those characteristic for pure nickel, evidencing a decrease of the number of unoccupied states, in Ni3d band.

The XPS valence bands, recorded on RNi$_3$ compounds, show that 4f orbitals keep their localized character and consequently the presence of multiplet structures—figure 2. The valence band spectra, in case of pure nickel show a main line at $\approx$0.6 eV binding energy. In case of RNi$_3$ compounds these lines are little shifted from the above value being now located at $\approx$0.7 eV. The 6 eV nickel satellite line in the valence band of RNi$_3$ compounds cannot be unambiguously observed due to superposition of R and Ni lines \[19\]. The, valence band spectra of RNi$_3$ compounds around E_F are somewhat similar to that of pure nickel, but the density of states at Fermi level, are diminished due to R5d-Ni3d hybridization effects.

The partial densities of states of the constituent atoms in GdNi$_3$ and Gd$_2$Ni$_{17}$ compounds, as determined by band structure calculations are given, for example, in figure 3. The nickel moments and R5d band polarizations,
theoretically determined, show interesting behaviour. The computed nickel moments in RNi₂, RNi₃, RNi₅ and 
R₂Ni₁₇ series follow linear dependences on De Gennes factor,

\[ G = (g_f - 1)J(J + 1), \]

with different rates for heavy (h) and light (l) rare-earth compounds—figures 4(a)–(d).

The ratio of the above rates, \( \alpha_h / \alpha_l \approx 1.6 \pm 0.1 \) seems to be not dependent on the nickel content in a given series. Consequently, for the same G value, the nickel moments are somewhat higher in compounds with light than in those with heavy rare-earths.

The MₙNi values, for a given RNiₙ (3 ≤ n ≤ 8.5) series, are dependent on site location, their local environment, respectively. In RNi₅ compounds, the higher Ni moment is located at 3g site, having R₃Ni₈ environment, decreasing at 2c site, where in their first coordination shell, R₃Ni₈, are only three R atoms. In R₂Ni₁₇ series, the Ni12k site having R₃Ni₉ coordination has the greater moment, the smaller one being located at Ni4f site with only one R atom (R₁Ni₁₃) in their nearest neighbour. These data evidence the part played by R atoms in inducing a magnetic moment on neighbour nickel atoms by 4f-5d-3d exchange path. More clear evidence on this effect can be seen in RNi₃ series. When R = Y which is non-magnetic, the MₙNi(6c) having R₃Ni₉ atomic environment is the highest one and the smaller at Ni(3b) with R₂Ni₆ atoms situated in their first coordination shell. When R is a magnetic rare-earth, this sequence is reversed.

The rates of MₙNi versus G dependences are also higher when the number of R atoms situated in the first coordination shell to a given Ni site is greater. Thus, in RNi₅ series, the \( dM_{Ni}(3g) / dG = 0.63 \cdot 10^{-2} \mu_B \), while \( dM_{Ni}(2c) / dG = 0.56 \cdot 10^{-2} \mu_B \). In R₂Ni₁₇ compounds with heavy rare-earths, rates \( dM_{Ni}(4f) / dG = 0.8 \cdot 10^{-3} \mu_B \) and \( dM_{Ni}(12k) / dG = 2.9 \cdot 10^{-3} \mu_B \), are obtained, confirming the part played by the R atoms in inducing an additional Ni moment. As a general trend, for all Ni sites, the mean \( dN_{Ni}/dG \) rates decrease as the nickel content, in a given series, is greater—figure 5.
The R5d bands are negatively polarized, their polarizations, \( M_{5d} \), in absolute magnitude, increasing linearly with De Gennes factor, G, with different rates for light \((l)\) and heavy \((h)\) rare-earths compounds—figures 4(a), (c), (d). As already reported \([17, 20]\), the \( M_{5d} \) values are determined by additive contributions of polarization, \( M_{5d}(f) \), resulting from 4f-5d local exchange and of \( M_{5d}(d) \) due to R5d-Ni3d short range interactions, hybridization effects, respectively:

\[
M_{5d} = M_{5d}(f) + M_{5d}(d)
\]

The linear dependences of \( M_{5d} \) versus G are due to \( M_{5d}(f) \) term, having different rates for light \((i = l)\) and heavy \((i = h)\) rare earth compounds.

\[
M_{5d}(f) = \beta_l G
\]

Not sensitive change in \( \beta_l / \beta_h \) ratio \((1.6 \pm 0.15)\) was shown, in the investigated RNi\(_2\), RNi\(_5\) and R\(_2\)Ni\(_{17}\), series. The above trend can be correlated with lanthanide contraction \([30]\). The radii of 4f shells \( r_{4f} \) in light rare-earths are in the range \(1.11\) Å \((R = \text{Pr})\) and \(0.98\) Å \((R = \text{Sm})\), while in heavy rare earths are significantly smaller, decreasing from \(0.85\) Å \((R = \text{Gd})\) to \(0.80\) Å \((R = \text{Dy})\) \([31]\). As a result, the exchange splitting of R5d band by 4f-5d local interaction, is significantly higher in nickel compounds with light rare-earths. Thus, for the same G value, a higher nickel moment is induced in compounds with light than in those with heavy rare-earths through R5d-Ni3d short range interactions. This mechanism explains also the different rates of the Curie temperatures for light and heavy rare-earth series, when plotting on De Gennes factor. The \( dM_{5d} / dG \) values follow the same trend as the mean \( dM_{5d} / dG \) rates in RNi\(_2\) series, evidencing the important part played by R5d band polarizations in mediating the exchange interactions in the spatial extension of the unit cell—figure 5.

The \( M_{5d}(d) \) contributions to R5d band polarizations, have been analysed starting from the Hamiltonian describing the interactions of R atom with their \( z_i \) Ni nearest neighbours. In the mean field model, \( M_{5d}(d) \) is proportional to the number \( z_i \) of Ni atoms situated in the first coordination shell to a given R atom as well as their magnetic moments \( M_{Ni} \) \([17, 20]\).

---

**Figure 3.** Partial densities of states for nickel and gadolinium in GdNi\(_2\) \((a, b)\) and Gd\(_2\)Ni\(_{17}\) \((c, d)\) compounds.
The $\gamma_i$ values, for a given series, determined at unequivalent R sites are rather close, these decreasing when increasing the nickel content—figure 5 inset. The $\gamma_i \cdot n$ product is only little dependent on the investigated RNin$_n$ series compositions.

The computed magnetic moments per formula unit were compared with experimental values. In addition to previous data [1, 3, 9, 17, 32, 33], magnetic measurements were also performed on SmNi$_5$ and R$_2$Ni$_{17}$ ($R = \text{Dy and Er}$) compounds. The saturation magnetizations, experimentally determined are rather close to the computed values, the mean differences being of the order of 5%.

\[ M_{3d}(d) = \gamma_i \sum z_i M_{Ni}^i \] (4)
The Curie temperatures of both light and heavy rare-earth-nickel compounds show the same trend, for a given series, when plotting as function of M5d values, confirming the important role of R5d band in mediating the exchange interactions—figure 6.

The M5d values are influenced by substitutions both at R and Ni sites, respectively. When a rare-earth, R, is partially replaced by another one, R′, in \( R_{n}Ni_{3n} \) series, the \( M_{5d}^{R}(f) \) and \( M_{5d}^{R′}(f) \) keep their values in the corresponding binary compounds, the mean polarization \( \langle M_{5d}(f) \rangle \) per formula unit, being given by the weighted average of those determined for R and R′ atoms \( \langle M_{5d}(f) \rangle = x M_{5d}^{R}(f) + (1 - x) M_{5d}^{R′} \), as for example in Gd\(_{1-x}\)La\(_{x}\)Ni\(_{5}\) series [33]. When Ni is replaced by another magnetic or non-magnetic element, the M5d(d) values are changed, according to relation (4), as evidenced YNi\(_{3-x}\)Co\(_{x}\) [34], NdNi\(_{5-x}\)Cu\(_{x}\) [19] or DyNi\(_{5-x}\)Al\(_{x}\) [17] pseudobinary compounds. The mean band polarizations \( \langle M_{5d} \rangle \) versus \( T_{c} \) in pseudobinary compounds follow the same trend as in the corresponding binary series—figure 6. These data are further support on the part played by R5d band polarizations in describing the exchange interactions within the spatial extension of the unit cell.

4. Conclusions

The XPS studies on RNi\(_{5}\) compounds suggest the presence of unoccupied Ni3d states. The densities of states at the Fermi level have mainly d character, being somewhat diminished as compared to that of Ni metal due to Ni3d-R5d hybridization. The band structure calculations show the presence of small nickel moments, for the RNi\(_{5n}\) (\( n = 2, 3, 3.5, 5 \) and 8.5) series, when R is a magnetic rare-earths. The nickel moments are dependent on the site location, their local environment, respectively. The R5d band polarizations mirror all the changes in magnetic properties, resulting from substitutions both at R and Ni sites. Further evidence for the part played by the R5d band polarizations in mediating the exchange interactions in binary and pseudobinary compounds, is given by the linear dependences of the Curie temperatures on M5d values, with the same rate for both heavy and light rare-earth compounds. The computed moments per formula unit agree rather well with those experimentally determined.

ORCID iDs

P Vlaic https://orcid.org/0000-0001-7104-1430

References

[1] Burzo E, Chelkowski A and Kirchmayr H R 1990 Landolt Bornstein Handbook (Verlag: Springer) 19d2
[2] Burzo E (ed) 2017 Hydrogen Storage Materials, Landolt Bornstein Handbook (Verlag: Springer)
[3] Yakinthos J K and Paccard D 1972 Solid State Commun. 10 989
[4] Yakinthos J K 1977 Phys. Stat. Soli(i) (B) 82 349
[5] Burzo E and Lafort J 1972 Int. J. Magn. 3 171
[6] Wallace W E and Aoyagi M 1971 Monats. Chem. 102 1455
[7] Lemaire R, Paccard D, Pauthenet R and Rend C 1967 Compte Rend. Acad. Sci. (Paris) B 265 1280
[8] Laforset J, Lemaire R, Paccard D and Pauthenet R 1967 Compte Rend. Acad. Sci. (Paris) B 264 676
[9] Burzo E and Laforset J 1972 Compte Rend. Acad. Sci. (Paris) B 274 114
[10] Mizumaki M, Yano R, Umehara I, Ishikawa F, Sato K, Koizumi A, Sakai N and Muro T 2003 Phys. Rev. B 67 132404
[11] Baer Y, Hedén P F, Hedman I, Klasson M, Nordlig C and Siegbahn K 1970 Solid State Commun. 8 517
[12] Hüfner S and Wertheim G K 1975 Phys. Lett. A 51 299
[13] Penn D R 1979 Phys. Rev. Lett. 42 921
[14] Liebsch A 1981 Phys. Rev. B 23 5283
[15] Hillebrecht F U, Fuggle J C, Bennett P A and Zolnierek Z 1983 Phys. Rev. B 27 2179
[16] Fuggle J C and Zolnierek Z 1981 Solid State Commun. 38 799
[17] Burzo E, Chiuzaiba S G, Neumann M, Valeanu M, Chioncel L and Creanga I 2002 J. Appl. Phys. 92 7362
[18] Bajorek A and Chelkowska G 2004 Molecular Phys. Repts. 40 50
[19] Burzo E, Crainic T, Neumann M, Chioncel L and Lazar C 2005 J. Magn. Magn. Mater. 290–291 371
[20] Burzo E, Chioncel L, Tetean R and Isnard O 2011 J. Phys.: Condens Matter 23 026001
[21] Campbell I A 1972 J. Phys. F.: Metal Phys. 2 L47
[22] Burzo E and Chioncel L 2018 Rom. J. Phys. 63 601
[23] Anderson O K 1975 Phys. Rev. B 12 3960
[24] Andersen O K and Jepsen O 1984 Phys. Rev. Lett. 53 2571
[25] Andersen O K, Jepsen O and Glosel D 1985 Highlight of Condensed Matter Theory ed F Bassani, F Fumi and M P Tosi (New York: North Holland)
[26] von Barth U and Hedin L 1972 J. Phys. C: Solid State 5 1629
[27] Anisimov V I, Aryasetiawan F and Lichtenstein A J 1997 J. Phys.: Condens. Matter 9 767
[28] Larson P, Lambrecht W R L, Chantini A and van Schilfgaarde W R L 2007 Phys. Rev. B 75 045114
[29] Yang I, Savrasov S Y and Kotliar G 2001 Phys. Rev. Lett. 87 216405
[30] Brooks M S S, Nordstrom I and Johansson B 1991 J. Phys.: Condens. Matter 3 2357
[31] vonsovski S V 1974 Magnetism (New York: Wiley)
[32] Burzo E, Takacs A, Neumann M and Chioncel L 2004 Phys. Stat. Soli (C) 1 3343
[33] Burzo E, Chioncel L, Costina I and Chiuzaiba S G 2006 J. Phys.: Condens. Matter 18 4861
[34] Burzo E, Deal I G, Tetean R and Creanga I 2008 Opt. Adv. Mater. Rapid Commun. 2 643

Mater. Res. Express 6 (2019) 126122 E Burzo and P Vlaic