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XPS study of $RNiSb_2$ (R = Pr, Nd)*

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The electronic structure of the ternary $RNiSb_2$ (R = Pr, Nd) compounds, which crystallize in the tetragonal primitive $ZrCuSi_2$-type structure, was studied by the X-ray photoemission spectroscopy. The R3d core-levels and the valence bands were investigated. The results for the $PrNiSb_2$ valence band are compared with the previously calculated density of states. The obtained results indicate that the valence bands are mainly determined by the Ni3d band. The analysis of the XPS spectra of $R3d_{5/2}$ and $R3d_{3/2}$ based on the Gunnarsson–Schönhammer model gives the hybridization of the 4f orbitals with the conduction band. The experimental data concerning the valence band of these compounds are compared with the calculations based on the KKR-CPA method. The calculated data for the room temperature (paramagnetic region) give the peaks corresponding to the R4f states at the Fermi level $E_F = 0$. A different distribution of the peaks corresponding to the Ni3d states is observed. For $PrNiSb_2$ three peaks at 2.0, 2.3 and 3.5 eV are observed while for $NdNiSb_2$ a broad maximum between 5.0 and 8.0 eV is visible. The experimental data for $PrNiSb_2$ are in good agreement with the calculated ones while those for $NdNiSb_2$ are not.

Key words: *electronic structure; rare earth intermetallics; photoemission spectroscopy*

1. Introduction

The compounds $RNiSb_2$ (R = Pr, Nd) crystallize in the tetragonal $ZrCuSi_2$-type structure (space group $P4/nmm$) [1, 2]. The atoms are located in the following positions: R atoms in 2(*c*): ¼, ¼, z_R, Ni atoms in 2(*a*): ¾,¼, 0 and 2(*c*): ¼, ¼, z_{Ni} and Sb atoms in 2(*b*): ¾, ¼, ½ and 2(*c*): ¼, ¼, z_{Sb}. Magnetic and neutron diffraction measurements give the Néel temperatures of 6.3 K for R = Pr and 2.3 K for R = Nd, re-

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spectively [3]. The neutron diffraction data at $T = 1.45$ K give the values of the magnetic moments lower than the free R^{3+} ions values.

In the course of systematic research of ternary rare earth intermetallic compounds we present the results of the photoemission measurements of $RNiSb_2$ compounds, where R = Pr and Nd. The XPS valence band spectra are compared with electronic structure calculations. Based on these results, the electronic structures of the compounds have been determined.

2. Experiment and results

All experiments were carried out on sintered pellets in vacuum. The XPS spectra were collected at room temperature using the Leybold LHS10 electron photoemission spectrometer with the MgK_α ($h\nu = 1253.6$ eV) and AlK_α ($h\nu = 1486.6$ eV) radiation in vacuum of about 10^{-9} mbar. The total energy resolution of the spectrometer with a hemispherical energy analyzer was about 0.75 eV for Ag3d. Binding energies were referred to the Fermi level ($E_F = 0$). The spectrometer was calibrated using the $Cu2p_{3/2}$ (932.5 eV), $Ag3d_{5/2}$ (368.1 eV) and $Au4f_{7/2}$ (84.0 eV) core-level photoemission spectra. Surfaces of the samples were mechanically cleaned by scraping with a diamond file in a preparation chamber under high vacuum (10^{-9} mbar) and then were moved immediately into the analysis chamber. This procedure was repeated until the C1s and O1s core-level peaks were negligibly small or were not changing after further scrapings. Such a cleaning procedure was performed before each XPS measurement. The Shirley method [4] was used to subtract background and the experimental spectra prepared in this way were numerically fitted using the 80% Gaussian and 20% Lorentzian model.

The electronic structure was calculated using the KKR–CPA method [5, 6]. The band structure was calculated using the specx (KKR–CPA) programme with the correlation – exchange potential proposed by Vosko et al. [7, 8]. Calculations were performed in the semi-relativistic treatment of the core level based on the available data on the crystal structure of $RNiSb_2$ (R = Pr, Nd): $a = 0.43674$ nm, $c = 0.9699$ nm, $z_R = 0.7635$, $z_{Ni} = 0.39$, $z_{Sb} = 0.125$ for R = Pr and $a = 0.45674$ nm, $c = 0.9629$ nm, $z_R = 0.7604$, $z_{Ni} = 0.38$, $z_{Sb} = 0.1345$ for R = Nd with the respective occupation numbers: 1 for R in 2*c*, $1 - n_{Ni}$ and n_{Ni} in 2*a* and 2*c* and 1 for Sb in 2*b* and 2*c*. The value of n_{Ni} is equal to 0.162 for R = Pr and 0.103 for R = Nd.

The calculated total density of states for $RNiSb_2$ (R = Pr, Nd) is shown in Fig. 1. The 4f level of Pr in $PrNiSb_2$ and of Nd in $NdNiSb_2$ gives high intensity peaks near the Fermi level. The observed distribution of the peaks corresponding to the Ni3d states is different: for $NdNiSb_2$ a broad maximum between 5.0 and 8.0 eV is visible. The data for the Pr compound are in good agreement with the previous calculations [9]. For $PrNiSb_2$ three peaks at 2.0, 2.3 and 3.5 eV are observed.

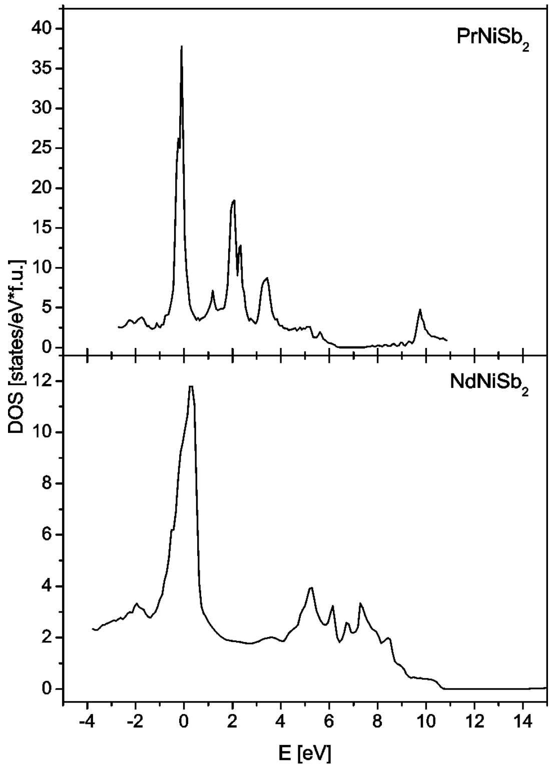

Fig. 1. Calculated electronic density of states for paramagnetic RNiSb$_2$ (R = Pr, Nd)

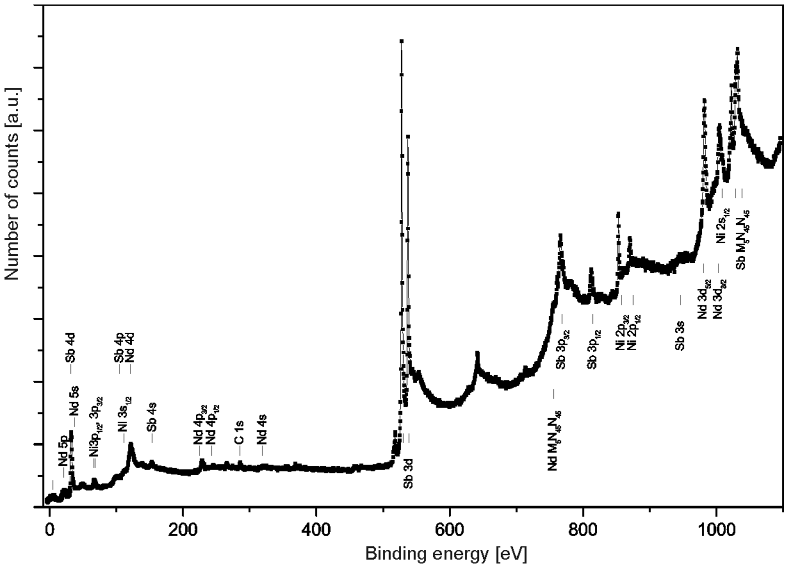

Fig. 2. XPS MgK$_\alpha$ spectrum of NdNiSb$_2$ (with the core-level lines)
in a wide binding energy range from 0 to 1100 eV

Figure 2 shows the XPS spectrum of the $NdNiSb_2$ compound in a wide binding energy range of 0–1100 eV. The binding energies are related to the Fermi level ($E_F = 0$).

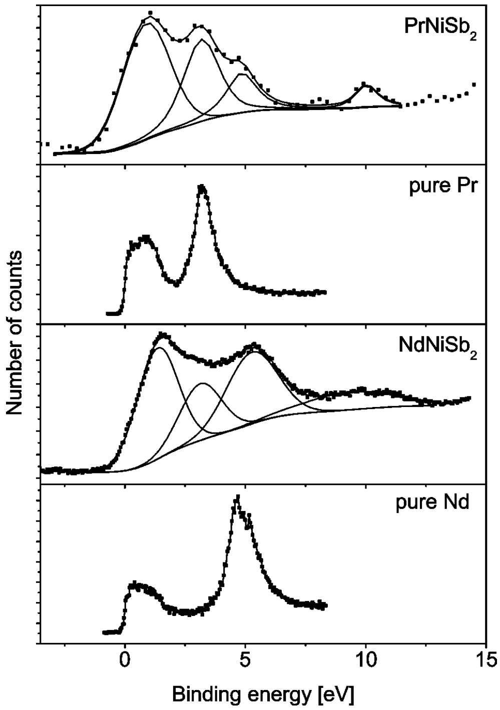

Fig. 3. XPS spectrum of valence band of $RNiSb_2$ (R = Pr, Nd) and the appropriate spectrum for metallic Pr and Nd

The XPS valence bands (VB) of $RNiSb_2$ (R = Pr, Nd) compounds and metallic Pr and Nd are presented in Fig. 3. In both $RNiSb_2$ spectra three peaks in the region between 0 and 7.5 eV and next at 10 eV are observed. Comparing the data for the investigated compounds and metallic rare earth elements with the calculations makes possible to give the interpretation of the measured spectra. The two peaks at 1.1 and 3.2 eV for $PrNiSb_2$ and 1.5 and 3.2 eV for $NdNiSb_2$ correspond to the Ni 3d states and the peak near 10 eV corresponds to the Sb 3s states. The peak connected with Pr 4f states in the $PrNiSb_2$ spectrum coincides with the second peak of the Ni 3d states at 3.2 eV. The peak of Nd 4f states in $NdNiSb_2$ spectrum is at 5.2 eV and is shifted to higher energies with respect to the metallic Nd (4.7 eV). The low intensity peak at 5.0 eV in $PrNiSb_2$ is probably connected with the oxygen impurity.

Figure 4 shows the Pr and Nd 3d XPS spectra of both investigated compounds. The high intensity peaks at 933.4 and 953.5 eV in $PrNiSb_2$ and 981.8 and 1004.6 eV in $NdNiSb_2$ correspond to the $R3d_{5/2}$ and $R3d_{3/2}$ levels. The structure of these spectra has been interpreted in terms of the Gunnarsson–Schönhammer theory [10]. The spin-orbit splitting corresponds to the spectral structure of the 3d XPS peaks. This splitting is equal to 20.1 eV for R = Pr and 22.8 eV for R = Nd. At low-binding-energy side of the $3d_{5/2}$ and $3d_{3/2}$ main lines the shake down satellites (at 929.0 and 948.8 eV for $PrNiSb_2$ and 978.3 and 1000.7 eV for $NdNiSb_2$) are observed which is known to account for the screened $Pr3d^94f^3$ and $Nd3d^94f^4$ final states [11]. The additional peaks at 925.1 and 945.4 eV for $PrNiSb_2$ and 973.5 and 996.1 eV for $NdNiSb_2$ are connected with the line corresponding to the parasite radiation ($K_{\alpha3}$, $K_{\alpha4}$). The peak at 964.7 eV in $PrNiSb_2$ is connected with the Pr Auger signal expected at this energy. The additional small intensity peaks at 983.7 and 1008.5 eV ($\Delta_{S\text{–}O}$ = 24.7 eV) correspond probably to the Nd atoms in the second site or to an impurity.

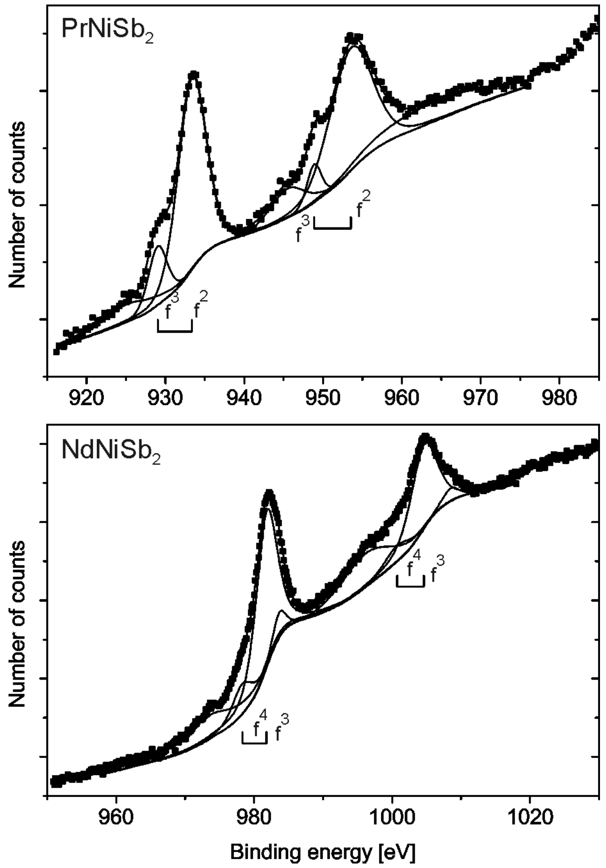

Fig. 4. X-ray photoemission spectra of $R3d_{5/2}$ and $R3d_{3/2}$ electron states of R = Pr, Nd in $RNiSb_2$ (R = Pr, Nd). The deconvolution of the spectra is shown. The strokes indicate the positions of the convoluted peaks (see the main text)

The energies and the relative intensities of R3d XPS peaks obtained as parameters which correspond to the final states in the fitting procedure are collected in Table 1. The separation of the peaks was based on the Doniach–Šunjić theory [12] which gives the intensity ratio $r = I(f^{n+1})/[I(f^n) + I(f^{n+1})]$. The relation between the r values and Δ parameters were calculated only for R = La and Ce [11]. The results [13] indicate that it is possible to estimate the values of Δ for R = Pr and Nd, based on this relation. However, the evaluated results are only qualitative. The coupling parameter Δ is defined as $\pi V^2\rho_{\max}$, where $\rho_{\max}$ is the maximum of the density of conduction states and V is the hybridization. The r values are 0.17 for $PrNiSb_2$ and 0.164 for $NdNiSb_2$ which corresponds to the hybridization energies of 82.5 and 80.5 meV, respectively.

Table 1. Binding energies (E) and relative intensities (I) of R3d XPS peaks for $PrNiSb_2$ and $NdNiSb_2$. All energies are given in eV and related to the Fermi energy level ($E_F = 0$)

Compound	$3d_{5/2}$	$3d_{3/2}$
$PrNiSb_2$		
E [eV]	925.1, 929.0, 933.4	945.4, 948.8, 953.5, 964,7
I	18.7, 20.2, 100	18.3, 13.5, 66.7, 36.4
$NdNiSb_2$		
E [eV]	973.5, 978.3, 981.8, 983.7	996.1, 1000.7, 1004.6, 1008.5
I	47.2, 19.6, 100, 9.4	42.4, 13.1, 66.7, 6.3

The data for $PrNiSb_2$ and $PrNi_{1.8}Sb_2$ give the values of r equal to 0.24 and 0.28 and the corresponding Δ values of 120 and 140 meV, respectively [14].

The $Ni2p_{3/2}$ peak in both compounds is observed at 853.0 eV below the Fermi level and has two additional satellites: 853.5 and 861.0 eV. These satellites have been observed in Ni metal, $TbNi_2Ge_2$ and Fe_2NiAl [15], $SmNi_2B$ [16] and U_2Ni_2In [17]. The existence of the satellites may suggest that the Ni 3d band is not completely filled [16, 18]. Because the intensity of the peaks in both compounds is smaller than that for the pure Ni metal one expects the Ni magnetic moment to vanish. This is in good agreement with the neutron diffraction data, which give no evidence for any magnetic moment localized on the Ni atoms [3].

3. Concluding remarks

The XPS spectra of $RNiSb_2$ (R = Pr, Nd) at room temperature and calculations of their electronic structure have been presented. The analysis of the $R3d_{5/2}$ and $R3d_{3/2}$ states indicates that the hybridization of the 4f and conduction states in both compounds is smaller than in $PrNi_{2-x}Sb_2$ ($\Delta \approx 120$, 140 meV) [14]. This result suggests strong localization of the R4f states in the $RNiSb_2$ (R = Pr, Nd) compounds. The analysis of the valence bands shows that Ni 3d peaks are close to the Fermi level, from which could be concluded that these states are mostly occupied. The XPS data give R4f states at 3.2 eV for Pr in $PrNiSb_2$ and 4.6 eV Nd in $NdNiSb_2$. These results suggest the hybridization of the R4f states and Ni 3d states which probably influence the values of the rare earth magnetic moments. The calculated value of the magnetic moment localized on praseodymium in $PrNiSb_2$, equal to $1.95\mu_B$ [9], is close to the experimental value ($1.88\mu_B$) [3]. Comparing our data for $PrNiSb_2$ with those presented in the work [19] for pure Pr and the oxides PrO_2 and Pr_2O_3 one can say that the effect of oxidation in our sample is small. Existence of a small oxygen impurity influences the intensity of the Pr3d-f^3 state and the value of the coupling parameter Δ that means that the obtained results are only quantitative.

The results presented in the paper give the explanation of the magnetic properties of the $RNiSb_2$ (R = Pr, Nd) compounds. The hybridization of Pr4f and Ni3d states cause the decrease of the value of the rare earth magnetic moment whereas small hybridization of Pr4f state with the conduction electron results in the low values of the Néel temperature. Similar properties are observed in the RAg_2Ge_2 (R = Pr, Nd) compounds which order at 12 K (R = Pr) and 2.0 K (R = Nd) and are characterized by low hybridization energies equal to 41 meV (R = Pr) and 71 meV (R = Nd) [20].

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