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Electronic structure of RTX (R=Pr, Nd; T=Cu, Ag, Au; X=Ge, Sn) compounds

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Abstract

Electronic structure of ternary RTX (R=Pr, Nd; T=Cu, Ag, Au; X=Ge, Sn) compounds was studied by X-ray photoemission spectroscopy. Core-levels and valence bands were investigated. The XPS valence bands are compared with the ones calculated using the spin-polarized tight binding linear muffin-tin orbital (TB LMTO) method. The obtained results indicate that the valence bands are mainly determined by Cu3d, Ag4d and Au5d bands. The spin–orbit splitting values ΔE_{LS} determined from the XPS spectra of Pr and Nd $3d_{5/2}$ and $3d_{3/2}$ are equal to 20.5 eV for Pr-compounds and 22.5 eV for Nd-compounds. The analysis of these spectra on the basis of the Gunnarsson–Schönhammer model gives a hybridization of f-orbitals with the conduction band.

Keywords: Electronic structure; Rare earth intermetallics; Photoemission spectroscopy

1. Introduction

Physical properties of RTX compounds with R=rare earth metals, T=nd transition metals and X=Si, Ge or Sn have been the subject of the intensive measurements lately [1]. For the time being, more than 1000 intermetallic RTX compounds are known [2]. They crystallize in more than 30 different crystal structures [3].

In this work the RTX compounds, where R=Pr, Nd; T=Cu, Ag, Au and X=Ge, Sn are investigated. These compounds crystallize in the hexagonal LiGaGe-type of structure [4–9] except for PrCuGe and NdCuGe which crystallize in a hexagonal AlB_2-type [7,10]. The magnetic data indicate that these compounds are antiferomagnets at low temperatures, except for PrAuGe which is a paramagnet up to 1.5 K [11].

The aim of this work is to study the electronic structure of RTX (R=Pr, Nd; T=Cu, Ag, Au; X=Ge, Sn) compounds by means of X-ray photoemission spectroscopy (XPS). The XPS valence band spectra are compared with ab initio electronic structure calculations using the tight-binding linear muffin-tin orbital method (TB LMTO) [12]. On the basis of these results the electronic structure of the compounds will be determined.

2. Experimental

All experiments were performed on sintered pellets in a vacuum of about 10^{-9} mbar.

The XPS spectra were obtained at room temperature using the Leybold LHS10 electron photoemission spectrometer with the MgKα ($h\nu$=1253.6 eV) and AlKα ($h\nu$=1486.6 eV) radiations. A total energy resolution of the spectrometer with a hemispherical energy analyser was about 0.75 eV for Ag 3d with MgK_α and about 0.8 eV for Ag 3d with AlKα. The binding energies are referred to the Fermi level (E_F=0).

The spectrometer was calibrated using the Cu $2p_{3/2}$ (932.5 eV), Ag $3d_{5/2}$ (368.1 eV) and Au $4f_{7/2}$ (84.0 eV) core-level photoemission spectra. Measurements were carried out at room temperature. Surfaces of the compounds were mechanically cleaned by scraping with a diamond file in a preparation chamber under high vacuum (10^{-9} mbar) and then, immediately moved into the analysis chamber. This procedure was repeated until the C 1s and O 1s core-level peaks were negligibly small or did not change after further scrapings. The procedure of cleaning was

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performed before each XPS measurement. The Shirley method [13] was used to substract the background and such prepared experimental spectra were numerically fitted using the 80% Gausiand and 20% Lorentzian model.

3. The method of calculation

The electronic structure was calculated by an ab-initio self-consistent tight binding linear muffin tin orbital method (TB LMTO) [8] within the framework of the local spin density approximation (LSD). The scalar-relativistic approximation for band electrons and the fully-relativistic treatment of the frozen core electrons were used. The exchange correlation potential was assumed according to von Barth and Hedin [14] with gradient corrections [15]. The self-consistent calculations were performed in the atomic sphere approximation (ASA) for the experimental value of the lattice parameters. We used 417 k-point in irreducible Brillouin zone. The values of the atomic sphere radii were chosen in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell. In the band calculations the initial atomic configurations were assumed according to the Periodic Table of Elements.

The theoretical photoemission spectra were obtained from the calculated density of states (DOS) convoluted by a Lorentzian line with a half-width equal to 0.4 eV and scaled using proper photoelectric cross sections for partial states [16].

4. Results and discussion

Fig. 1 shows the XPS photoemission spectra of some of these compounds (PrAuSn and NdCuSn) in a wide binding energy range 0–1100 eV. Binding energies are related to the Fermi level ($E_F=0$). A small oxygen and carbon contamination is visible.

4.1. XPS valence band

The XPS valence bands (VBs) of PrTX and NdTX (T=Cu, Ag, Au; X=Ge, Sn) compounds are shown in Fig. 2. The bands extend from the Fermi energy, located at $E=0$, to the binding energy of 14 eV. The obtained experimental data are compared with the calculated ones. In Fig. 3 we present for example the calculated partial and total densities of states (DOS's) for PrAgSn and NdAgSn compounds. A comparison of these data and the data for RAuGe compounds from Refs. [17,18] indicates that the valence bands of the compounds are dominated by the contribution of Cu3d, Ag4d and Au5d states.

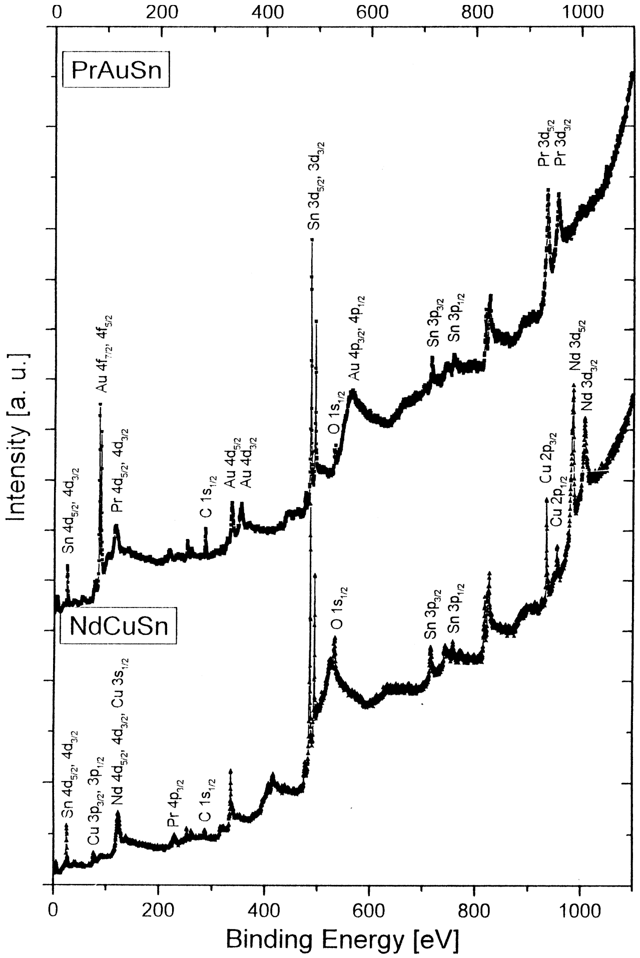

Fig. 1. XPS MgKα spectra for PrAuSn and NdCuSn compounds.

A detailed analysis of the valence band gives the following information:

- near 1 eV above the Fermi level there is located the $(6s5d)^3$ band. It forms a conduction band,
- the XPS Cu 3d band in PrCuSn is one broad peak at 4.2 eV while for NdCuGe and NdCuSn two peaks at 4.2 and 5.4 for NdCuGe and 4.3 and 6.1 eV for NdCuSn. The calculated data give only one peak at 3.2 eV for PrCuGe and NdCuGe, 2.9 eV for NdCuGe and 2.8 eV for NdCuSn.
- the Ag 4d band in PrAgSn and NdAgSn is near 6.0 eV. The experimental values agree with the calculated data (5.6 eV), however, the splitting of the $4d_{3/2}$ and $4d_{5/2}$ states obtained in experiments (1.7 eV for PrAgSn and 1.3 eV for NdAgSn) are larger than calculated (0.2–0.3 eV). For metallic Ag the splitting ΔE is 1.7 eV[1],
- the Au 5d band in RAuGe and RAuSn is represented by two peaks. The experimental values of the splitting of

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[1] These data are obtained from the measurements for pure Ag and Au metal.

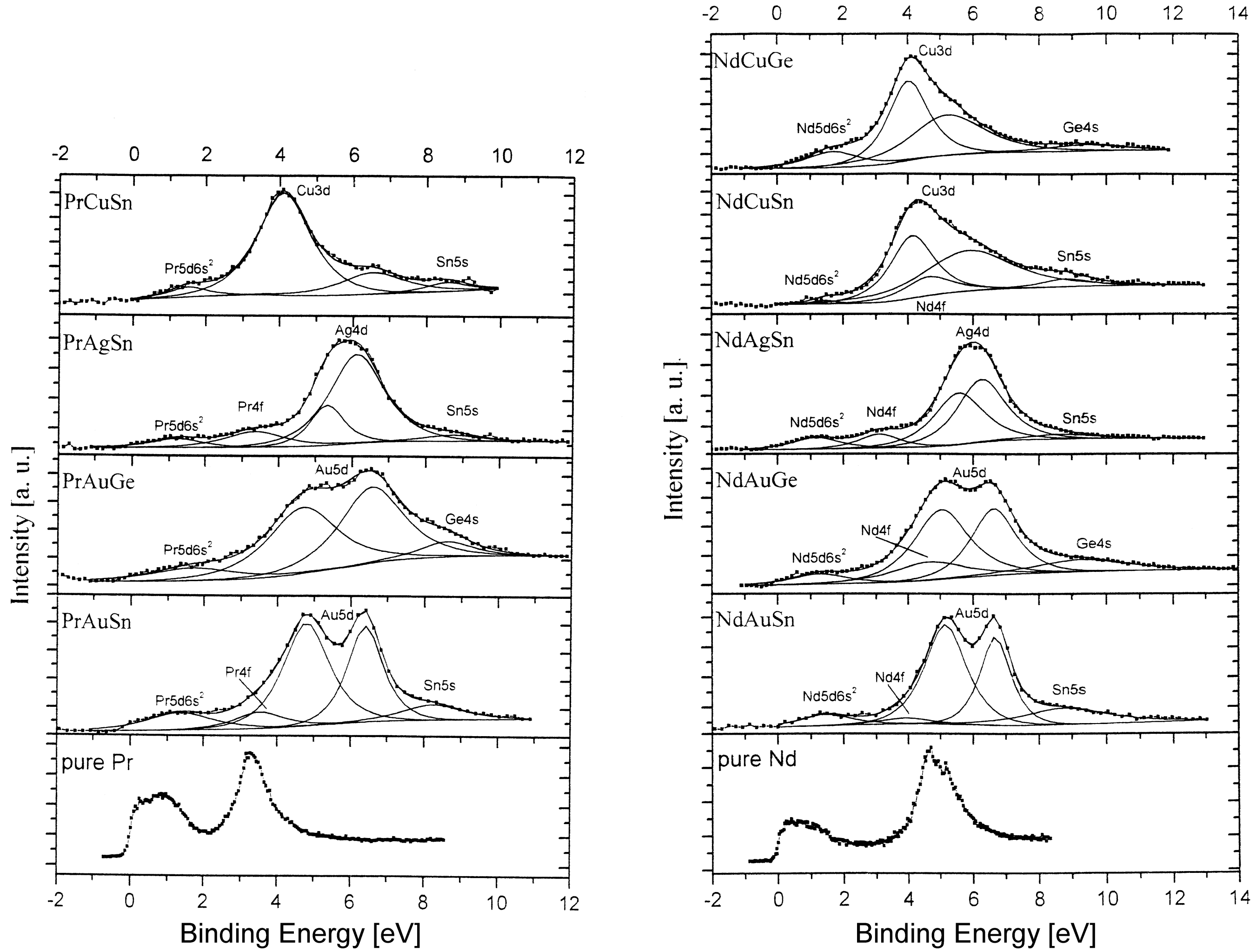

Fig. 2. XPS spectra of valence bands in (a) PrTX and (b) NdTX (T=Cu, Ag, Au; X=Ge, Sn) compounds and the appropriate spectra for metallic Pr and Nd taken from [19].

these peaks equal 2.0 eV for PrAuGe, 1.6 eV for PrAuSn and 1.5 eV for NdAuGe and NdAuSn are bigger than calculated 0.7 eV for PrAuGe and PrAuSn and 1.3 eV for NdAuGe and NdAuSn, and they are smaller than that observed in metallic Au (3.0 eV)[1],

- the position of Pr 4f bands are determined at 3.5 eV for some Pr-compounds and Nd 4f band at 4.5 eV for Nd-compounds. The positions of these peaks are in agreement with the ones obtained for pure metals [19],
- the broad Ge 4s and 5s bands of a small intensity are above 8.0 eV.

4.2. Core levels

The energy value of core levels are listed in Tables 1 and 2. The determined values are near to the values for pure elements from Ref. [20].

Fig. 4 illustrates the Pr and Nd 3d XPS spectra of the investigated compounds. The spin–orbit splitting dominates the spectral structure of 3d XPS peaks of Pr and Nd atoms. The 3d spin–orbit splitting in these compounds is equal to 20.5 eV for R=Pr and 22.5 eV for R=Nd (see Table 3). At the low-binding-energy side of the $3d_{5/2}$ and $3d_{3/2}$ main lines there are satellites which result from the screened Pr3d^{9}4 f^3 and Nd3d^{9}4 f^4 final states [21]. The additional small peaks correspond to Pr_2O_3 and Nd_2O_3 impurity [22,23].

The structure of these XPS spectra was interpreted in terms of the Gunnarsson–Schönhammer theory [21]. This theory used in the XPS Ce-spectra calculations showed how experimental spectra can be used to estimate f-occupancy, n_f, and the coupling, Δ, between the f-orbitals and the conduction states.

In Fig. 4 the Pr and Nd $3d_{5/2}$ XPS spectra overlap. Their separation on the basis of the Doniach–Šunjií theory [24] gives the intensity ratio $r = I(f^{n+1})/\{I(f^n) + I(f^{n+1})\}$

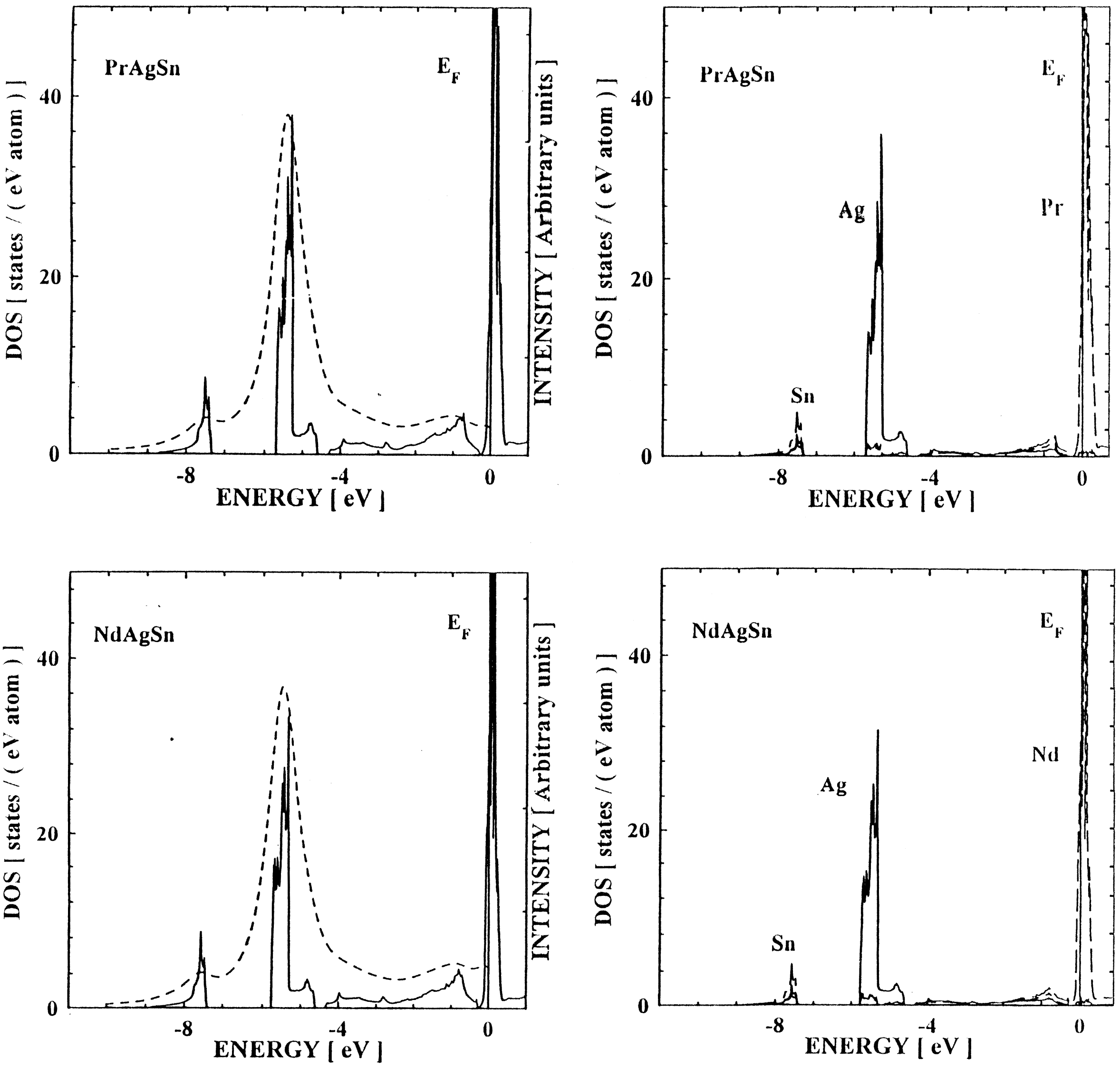

Fig. 3. The total density of states and the contribution from Pr or Nd (6s, 6p, 5d and 4f electrons), Ag and Sn to the total density of states for paramagnetic PrAgSn and NdAgSn. The Fermi level is located at $E=0$ eV. The dashed lines present the density of states convoluted by Lorenzians of half-width 0.4 eV and multipled by the appropriate cross section [16].

which is shown in Table 3. The intensity ratio r as a function of Δ is calculated for R=La and Ce [25]. 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. On the basis of this dependence a crude estimation of Δ for Pr and Nd ions seems to be possible if one assumes [26] that for Pr and Nd the calculated intensity ratio r changes with Δ in the same way as in the case of Ce [25]. The determined values of r and corresponding values of Δ parameters are listed in Table 3. The data presented in Table 3 indicate that in these compounds with an increase in the number of the nd-electrons ($n=3$, 4, 5) the value of the Δ parameter decreases. The decrease of the Δ parameter is connected with an increase of the Néel temperature.

For the same T element the Δ parameter is higher for stannides than germanides while the Néel temperature is lower for stannides.

5. Conclusions

The XPS measurements and calculations of electronic structure were performed for the RTX (R=Pr, Nd; T=Cu, Ag, Au; X=Ge, Sn) series of compounds. They lead to the following conclusions:

1. The valence bands are dominated by contribution of Cu 3d, Ag 4d and Au 5d states. The calculated density of states (using the LMTO method) is comparable with the experimental one.

Table 1
Comparison of the binding energies in eV obtained for PrTX compounds with the table data from Ref. [20]

Element	Level	Table data from Ref. [20]			Experimental values of the binding energies in eV *PrTX*			
					PrCuSn	PrAgSn	PrAuSn	PrAuGe
Pr	5p$_{1/2}$		22.3		19.3	21.4	18.6	19.9
	5p$_{3/2}$							23.8
	4d$_{3/2}$		115.1		116.6	115.9	115.9	116.0
	4d$_{5/2}$							
	3d$_{5/2}$		928.8		933.7	933.4	933.5	933.9
	3d$_{3/2}$		948.3		953.9	954.0	953.9	954.4
		Cu	Ag	Au				
T = Cu, Ag, Au	3s	122.5			122.6			
	3d$_{5/2}$	932.5	368.1		933.7	368.8		
	3d$_{3/2}$	952.5	374.0		953.9	374.8		
	5p$_{1/2}$			74.2			76.5	76.5
	4f$_{7/2}$			84.0			84.8	84.8
	4f$_{5/2}$			87.8			88.5	88.4
	5s			107.2			102.6	109.7
	4p$_{5/2}$			335.1			336.0	336.9
	4p$_{3/2}$			353.2			354.0	354.7
		Sn		Ge				
X = Sn, Ge	4d$_{5/2}$	23.8			24.0	23.6	23.9	
	4d$_{3/2}$	24.8			25.1	24.6	25.0	
	4s	137.1			136.5	135.9	136.6	
	3d$_{5/2}$	484.9		29.2	485.0	484.7	485.1	29.8
	3d$_{3/2}$	493.1		29.9	493.5	493.2	493.5	30.1
	3p$_{3/2}$			120.8				121.6

Table 2
Comparison of the binding energies in eV obtained for NdTX compounds with the table data from Ref. [20]

Element	Level	Table data from Ref. [20]			Experimental values of the binding energies in eV				
					NdCuSn	NdAgSn	NdAuSn	NdCuGe	NdAuGe
Nd	5p$_{1/2}$		21.1		19.9	18.8	19.8	19.6	19.6
	5p$_{3/2}$								
	4p$_{3/2}$		225.0					229.1	229.2
	4d$_{3/2}$		120.5		122.5	121.3	121.5	122.3	121.5
	4d$_{5/2}$					125.0	125.6	125.6	
	3d$_{5/2}$		980.4		982.8	982.7	982.5	982.6	982.4
	3d$_{3/2}$		1003.3		1005.4	1005.2	1004.9	1005.0	1005.0
		Cu	Ag	Au					
T = Cu, Ag, Au	3s	122.5			122.5			122.3;	
	2p$_{3/2}$	932.5			933.5			933.4	
	2p$_{1/2}$	952.5			953.4			953.4	
	3d$_{5/2}$		368.1			368.9			
	3d$_{3/2}$		374.0			374.9			
	5p$_{1/2}$			74.2			76.5		76.6
	4f$_{7/2}$			84.0			85.0		84.9
	4f$_{5/2}$			87.8			88.7		88.6
	5s			107.2			102.7 (99.2)		107.8
	4p$_{5/2}$			335.1			336.4		336.0
	4p$_{3/2}$			353.2			354.3		353.9
		Sn	Ge						
X = Sn,Ge	4d$_{5/2}$	23.8			24.3	23.7	24.2		
	4d$_{3/2}$	24.8			25.3	24.8	25.2		
	4s	137.1			137.3	135.5	137.1		
	3d$_{5/2}$	484.9	29.2		485.1	485.0	485.2	29.1	29.1
	3d$_{3/2}$	493.1	29.9		493.6	493.4	493.7		
	3p$_{3/2}$		120.8					122.3	121.5
	3p$_{1/2}$		124.9					125.6	124.5; 126.8
	3s		180.1					180.7	181.1

Table 3
Values of the energy levels [in eV] of $3d_{5/2}$ and $3d_{3/2}$ Pr and Nd, and respective value of the spin–orbit splitting energy ΔE_{LS}, the intensity ratio r and coupling energy Δ and Néel temperature of RTX and NdTX compounds[a]

Compound	$E(3d_{3/2})$ [eV]		$E(3d_{5/2})$[eV]		E_{LS} [eV]	$r(d_{5/2})$	Δ [meV]	T_N [K]
	f^n	f^{n+1}	f^n	f^{n+1}				
NdCuSn	1005.3	1000.8	982.8	978.8	22.5	0.168	82.8	10.0
NdAgSn	1005.2	1000.5	982.6	978.6	22.6	0.122	62.5	11.5
NdAuSn	1004.9	997.9	982.5	978.3	22.4	0.064	32.8	14.0
NdCuGe	1005.0	1000.0	982.6	978.7	22.4	0.147	75.0	3.5
NdAuGe	1005.0	1000.6	982.4	978.3	22.6	0.052	25.0	8.8
PrCuSn[b]	953.9	948.7	933.7	929.0	20.2	0.100	50.0	3.0
PrAgSn	954.0	949.2	933.4	929.0	20.6	0.158	78.1	3.8
PrAuSn	953.9	949.3	933.5	929.1	20.4	0.090	43.8	3.5
PrAuGe	954.7	949.8	934.1	931.8	20.6	0.055	28.1	

[a] $E(3d_{3/2})$, energy of $3d_{3/2}$ level; $E(3d_{5/2})$, energy of $3d_{5/2}$ level; and T_N, Néel temperatures.
[b] Observed apostasy for PrCuSn compound is cause by overlaping of Pr 3d and Cu 2p levels.

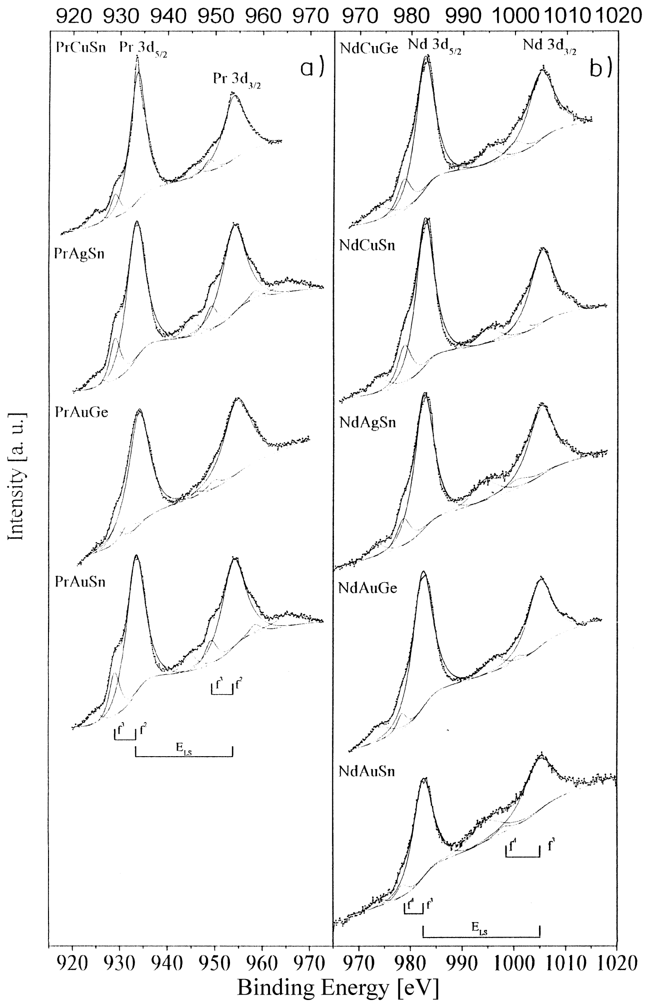

Fig. 4. X-ray photoemission spectra of $3d_{5/2}$ and $3d_{3/2}$ electron states Pr and Nd in PrTX and NdTX (T=Cu, Ag, Au; X=Ge, Sn) compounds.

2. The energy value of core levels are near to the values for pure elements.
3. The spin–orbit splitting is dominates the spectral structure of 3d XPS peaks of Pr and Nd atoms. The values of the spin–orbit splitting is equal to 20.5 eV for Pr and 22.5 eV for Nd-compounds.
4. The hybridization (coupling energy Δ) experimentally determined from the intensity ratio r based on the Gunnarsson–Schönhammer model decrease with increase of number of the nd-electrons and decrease with an increase in the number of 4f electrons.

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