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Electronic structures of intermetallic rare earth compounds

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The electronic structures of intermetallic rare earth compounds of different compositions: RMn_2Ge_2 (R = Nd, Sm), $R_3Mn_4Sn_4$ (R = La, Ce, Nd), $Ce_3Ag_4X_4$ (X = Ge, Sn), and Ce_2MnGe_6, have been investigated. XPS measurements were performed using a commercial LHS10 spectrometer. The valence band and core-level states have been analysed. In Mn compounds, the Mn 3d state forms a broad band near the Fermi level. The analysis of XPS spectra using the Gunnarsson–Schönhammer model gives the coupling parameters (hybridisation energy) between the R 4f states and electrons of the conduction band.

Key words: *rare earth compounds; transition metal compounds; electronic structure; photoelectron spectroscopy*

1. Introduction

The magnetic properties of ternary rare earth transition metal silicides, germanides, and stannides have been intensively studied over the last 30 years. Among these compounds, special attention is drawn by those of the R–Mn–X system in which it is expected that both rare earth and Mn atoms have localized magnetic moments. In this work, the electronic structures of compounds with Mn and isostructural compounds without Mn–RMn_2Ge_2 (R = Nd, Sm), RAg_2Ge_2 (R = Pr, Nd), $R_3Mn_4Ge_4$ (R = La, Ce, Nd), $Ce_3Ag_4X_4$ (X = Ge, Sn), and Ce_2MnGe_6 are investigated in order to determine their electronic structure. The valence band state and core-level states are also analysed.

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RMn_2Ge_2 (R = Nd, Sm) and RAg_2Ge_2 compounds crystallize in the tetragonal $ThCr_2Si_2$-type structure [1, 2]. In RMn_2Ge_2 compounds, the rare earth magnetic moments (Nd, Sm) order at low temperatures, whereas the Mn moments order close to 300 K [1]. $PrAg_2Ge_2$ remains paramagnetic down to 1.9 K, $NdAg_2Ge_2$ is an antiferromagnet at low temperatures [3], and Ce_2MnGe_6 is a ferrimagnet.

$R_3Mn_4Sn_4$ and $Ce_3Ag_4X_4$ compounds crystallize in an orthorhombic crystal structure of the $Gd_3Cu_4Ge_4$-type [4, 5]. In $R_3Mn_4Sn_4$, the Mn moments order at about room temperature, whereas the rare earth moments order at low temperatures [5]. In $Ce_3Ag_4X_4$ magnetic order is found at low temperatures.

2. Experimental and results

XPS spectra were obtained at room temperature using a Leybold LHS10 electron photoemission spectrometer with MgK_α ($h\nu$ = 1253.6 eV) and AlK_α ($h\nu$ = 1486.6 eV) radiation. All experiments were performed 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 Ag 3d. Binding energies are given relative to the Fermi level ($E_F = 0$). The spectrometer was calibrated using 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. The 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 moved immediately to the analysis chamber. This procedure was repeated several times until the C 1s and O 1s core-level peaks became negligibly small or did not change after further scrapings. Such a cleaning procedure was performed before each XPS measurement. The Shirley method [6] was used to subtract background and the experimental spectra prepared in this manner were numerically fitted using the 80% Gaussian and 20% Lorentzian model.

The XPS spectra of the investigated compounds were measured over a wide binding energy range of 0–1100 eV. The binding energies were related to the Fermi level ($E_F = 0$ eV). The XPS valence bands (VB) of some of the investigated compounds are presented in Fig. 1.

The valence bands of all the Mn compounds have a similar character. The Mn 3d state forms a broad band near the Fermi level. The R 4f state, where R is a light rare earth element, forms a narrow band at 3 eV below E_F for R = Pr, and at 5 eV for R = Nd and Sm. In RAg_2Ge_2 and $Ce_3Ag_4X_4$, the valence bands are dominated mainly by broad peaks near 5.8 eV, corresponding to Ag $4d_{3/2}$ and Ag $4d_{5/2}$ sites. A very weak peak near the Fermi level at ca. 1.2 eV, corresponding to the $(5d6s)^3$ state, is present. In $Ce_3Ag_4X_4$, an additional peak near 2.5 eV, corresponding to the Ce $4f^1$ state, is observed. In RAg_2Ge_2 compounds, the peaks corresponding to Pr 4f and Nd 4f coincide with the Ag 4d band. In all the investigated germanides the Ge 4p and 4s bands, and for the stannides the Sn 5p and 5s bands, form broad bands, which coincide with the states of 4f- and nd-electron elements. These results indicate the existence of a direct charge transfer from Ge or Sn to Mn.

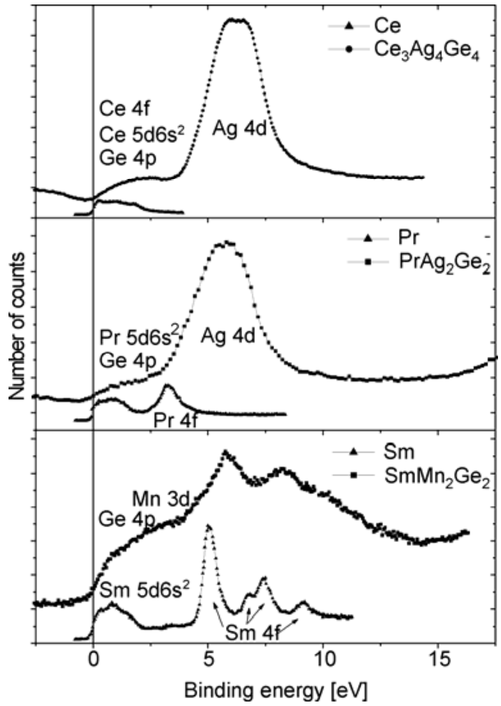

Fig. 1. XPS valence band spectra of $Ce_3Ag_4Ge_4$, $PrAg_2Ge_2$, and $SmMn_2Ge_2$ compared to those of the pure elements [11]

For example, Figure 2 shows the R $3d_{5/2}$ and R $3d_{3/2}$ core-levels for $Ce_3Ag_4Ge_4$, $PrAg_2Ge_2$, and $SmMn_2Ge_2$. Similar patterns are observed for the other investigated compounds. The spin-orbit splitting, $\Delta_{S\text{–}O}$, dominates the spectral structure of the 3d peaks. The determined values are listed in Table 1. The obtained values of $\Delta_{S\text{–}O}$ are independent of composition and increase with the increasing number of 4f electrons.

An analysis of the XPS spectra of R $3d_{5/2}$ and R $3d_{3/2}$ states based on the Gunnarsson-Schönhammer model [7] provides information on the hybridisation of 4f orbitals with the conduction band. The separation of the peaks based on Doniach–Šunjić theory [8] gives the ratio of $r = I(f^{n+1})/[I(f^n) + I(f^{n+1})]$. From the ratio r, it is possible to estimate the coupling parameter Δ. The coupling parameter Δ is defined as $\pi V^2\rho_{\max}$, where $\rho_{\max}$ is the maximum density of states of the conduction electrons and V is the hybridisation matrix. On the basis of the Gunnarsson–Schönhammer model, an estimation of Δ for Pr, Nd, and Sm compounds seems to be possible if one assumes that their calculated intensity ratios r change with Δ in the same way as for Ce [9, 10]. The determined values of the ratio r and adequate values of the coupling parameter Δ are summarized in Table 1.

The coupling parameter Δ has large values for the cerium compounds, particularly for those containing also manganese atoms. In this case, $\rho_{\max}$ attains large values, because the Mn 3d band is at the Fermi level and the hybridisation energy between the Ce 4f states and conduction band is large. The density of states on the Fermi level for the isostructural RMn_2Ge_2 (R = La, Y) compounds are 2.8 and 1.47 states/eV·atom, respectively [9]. The calculated Mn magnetic moments for these compounds are near $3.0\mu_B$, which is in good agreement with the Mn moment found in the compounds investigated here. The Mn 2p core-level spectra for RMn_2Ge_2 (R = Nd, Sm), $R_3Mn_4Sn_4$ (R = La, Ce, Nd), and Ce_2MnGe_6 have a similar character. The spin-orbit splitting of

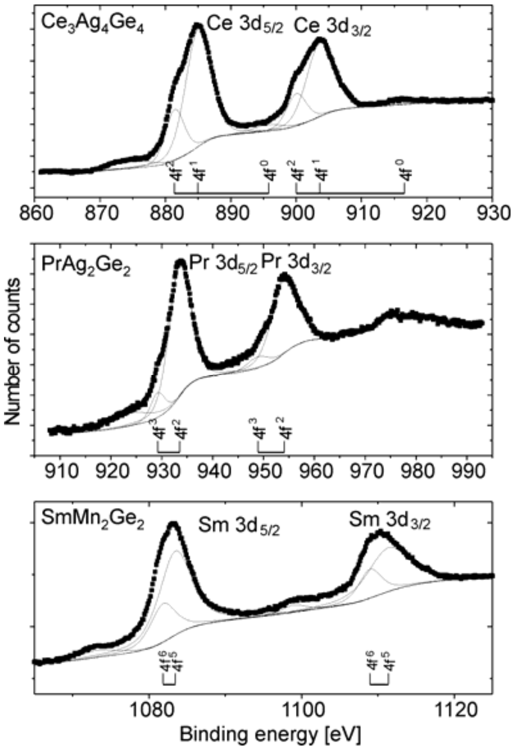

Fig. 2. 3d XPS spectra of $Ce_3Ag_4Ge_4$, $PrAg_2Ge_2$, and $SmMn_2Ge_2$. The broad, low intensity peaks, observed at 874 and 896 eV for $Ce_3Ag_4Ge_4$, 923 eV for $PrAg_2Ge_2$, and 1068 and 1098 eV for $SmMn_2Ge_2$, correspond to the $K\alpha_3$ and $K\alpha_4$ components of the X-ray radiation

Table 1. The values of r and corresponding hybridisation energy Δ

Compound	Δ_{S-O} (meV)	r	Δ (meV)	μ_{Mn} [μ_B]
$NdMn_2Ge_2$	22.4	0.07	37.5	2.7
$SmMn_2Ge_2$	27.4	0.18	80.0	3.0
$PrAg_2Ge_2$	20.5	0.09	58.0	
$NdAg_2Ge_2$	21.1	0.17	75.0	
Ce_2MnGe_6	18.7	0.25	126.0	2.0
$Ce_3Mn_4Sn_4$	19.0	0.35	186.0	
$Nd_3Mn_4Sn_4$	21.8	0.27	133.0	3.20(6)
$Ce_3Ag_4Ge_4$	18.7	0.33	169.0	
$Ce_3Ag_4Sn_4$	18.6	0.165	82.0	

the Mn 2p levels is between 10.9 and 11.6 eV, typical of Mn compounds. The values for RAg_2Ge_2 (R = Pr, Nd) indicate the weakness of the coupling of 4f electrons and condition band electrons, which manifests itself in the magnetic properties of these compounds.

In the $Ce_3Ag_4X_4$ (X = Ge, Sn) compounds an additional peak, corresponding to the $3d^94f^0$ configuration of the cerium ion, is observed. Based on the Gunnarsson –Schönhammer model [7], the intensity ratio $I(f^0)/[I(f^0)+I(f^1)+I(f^2)]$ which is directly related to the probability of f-occupation in the final state, reflects the f-occupation number n_f. The occupation number of the f shell, n_f, is equal to 0.95 for $Ce_3Ag_4Ge_4$ and 0.97 for $Ce_3Ag_4Sn_4$, which suggests the intermediate valence behaviour of Ce in these compounds.

The results obtained indicate a strong hybridisation of the 4f and conduction electrons in cerium compounds. This influences the Ce magnetic moment and other properties of the studied compounds. For Mn-compounds, the broad state of Mn 3d determines the magnetic moment and magnetic properties of these compounds.

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