Magnetic And Electronic Structure Of Rare Earth Intermetallic Compounds

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Abstract. In the work the influence of the electronic structure on the magnetic properties of some rare earth intermetallic compounds is discussed. The XPS spectroscopy data indicate that in YbMn₂Si₂ the Yb³⁺ ion is magnetic while in YbMn₂Ge₂ the Yb²⁺ ion is nonmagnetic. The valence state strongly influences on the magnetic properties of these compounds at low temperatures. The analysis of the XPS spectra of Pr and Nd 3d⁵/₂ and 3d³/₂, on the basis of the Gunnarsoon-Schönhammer model, gives the information on the hybridization of the 4f orbital with the conduction band. The large value of the hybridization energy obtained for PrPdSb explains the absence of the ordered magnetic moment at the Pr sites in this compound.

1. INTRODUCTION

Magnetic properties of rare earth ternary intermetallic compounds have been the subject of intensive research. It is generally accepted that the collective behavior of the magnetic rare earth ions in these compounds is determined by an indirect interaction between localized f electrons coupled by the conduction electrons according to the Ruderman-Kittel-Kasuya-Yosida (RKKY) theory [1, 2]. In the RKKY theory the exchange integral J(R) is proportional to the density of electronic states at the Fermi level. The characteristics of rare earth intermetallics are determined by the electronic structure of individual constituents, the crystal structure and symmetry. Large diversities in materials properties are realized due to differences in the electronic structure. To investigate the influence of the electronic structure on the magnetic properties, the results of magnetic and neutron diffraction investigations are compared with the photoemission spectroscopy data.

2. RESULTS

2.1. YbMn₂X₂ (X= Si, Ge)

The YbMn₂X₂ (X= Si, Ge) compounds crystallize in the tetragonal ThCr₂Si₂-type structure (bct; space group I4/mmm). Both compounds are antiferromagnets. The magnetic and the ⁵⁷Fe Mössbauer spectroscopy measurements of pure and ⁵⁷Fe doped samples of YbMn₂Si₂ give an additional phase transition at 35 K [3]. The neutron diffraction data [4] show that YbMn₂Si₂ has a collinear antiferromagnetic structure with the Mn moments parallel to the c-axis below the Néel temperature of 526(4) K. Below Tᵣ~30(5) K the Mn sublattice rearranges into the + − − + antiferromagnetic...
structure with the propagation vector \( \mathbf{k} = (0, 0, \frac{1}{2}) \). At lower temperatures (\( T < 10 \) K) the antiferromagnetical order with the propagation vector \( \mathbf{k} = (0, 0, \frac{1}{2}) \) is detected in the Yb sublattice (the same \( \mathbf{k} \) as in the Mn sublattice).

The magnetic and \(^{57}\text{Fe} \) Mössbauer spectroscopy data of YbMn\(_2\)Ge\(_2\) indicate the Néel temperature at \( 495(5) \) K and two further phase transitions at \( 190(10) \) and \( 350(10) \) K \[5\]. The neutron diffraction data show that YbMn\(_2\)Ge\(_2\) has a planar antiferromagnetic structure below \( T_N = 510 \) K and a canted antiferromagnetic structure below \( T_c \sim 185 \) K. No evidence for any magnetic ordering in the Yb lattice is obtained down to \( 1.5 \) K \[5\].

To explain the difference in the magnetic properties of the Yb sublattice the XPS measurements for both compounds were carried out. The XPS valence bands between the Fermi energy \( (E_F=0 \) eV) and the binding energy for both compounds and for metallic Yb and Mn are shown in Fig. 1a. The obtained results lead to different valence bands for these compounds. In the case of YbMn\(_2\)Si\(_2\) near the Fermi level only a broad maximum corresponding to the Mn3d states was detected between \( E_F \) and 3.0 eV while between 5 and 12.5 eV the peaks corresponding to Yb\(^{3+}\) were observed. For YbMn\(_2\)Ge\(_2\) two peaks similar to those in the metallic Yb, corresponding to the Yb\(^{2+}\) ions, are present near the Fermi level.

The Yb4d XPS spectra of both investigated compounds and the metallic Yb are collected in Fig. 1b. For the metallic Yb and YbMn\(_2\)Ge\(_2\) two peaks corresponding to the Yb4d\(_{5/2}\) and 4d\(_{3/2}\) spin-orbit splitting for Yb\(^{2+}\) are observed. The YbMn\(_2\)Si\(_2\) spectrum shows a very complex structure corresponding to the Yb\(^{3+}\) ions.

![FIGURE 1.](image-url) (a) XPS spectra of valence bands in YbMn\(_2\)X\(_2\) (X= Si, Ge) and the appropriate spectra for metallic Yb and Mn. (b) Yb 4d core level photoemission spectra for YbMn\(_2\)X\(_2\) (X= Si, Ge) and metallic Yb.

The Mn magnetic moments calculated on the basis of these data are equal to 1.93 \( \mu_B \) for YbMn\(_2\)Si\(_2\) and 2.34 \( \mu_B \) for YbMn\(_2\)Ge\(_2\) \[6\] while the values determined from the neutron diffraction experiments are 1.98(7) \( \mu_B \) \[4\] and 3.03(5) \( \mu_B \) \[5\], respectively.
2.2. RPdSb (R= Pr, Nd)

RPdSb (R= Pr, Nd) compounds crystallize in the hexagonal LiGaGe-type structure. NdPdSb is an antiferromagnet with the Néel temperature equal 10 K while for PrPdSb the neutron diffraction measurements indicate the absence of any long-range magnetic order down to 1.5 K [7]. Fig. 2a shows the XPS valence bands of PrPdSb, NdPdSb and of pure Pr, Nd and Pd. The presented results indicate that the valence bands of PrPdSb and NdPdSb are mainly determined by the Pd 4d band. The valence band spectra show that the Fermi level is getting narrow and moves away (GFWHM= 2.3 eV, BE= 3.7 eV for PrPdSb and GFWHM= 2.2 eV, BE= 4.4 eV for NdPdSb) in comparison with the pure Pd (GFWHM= 4.1 eV, BE= 1 eV). These results suggest the filling of the Pd states of the investigated compounds by the transfer of s electrons.

![FIGURE 2. XPS spectra of (a) valence bands of RPdSb (R = Pr, Nd) and pure Pd. The spectra of RPdSb (R = Pr, Nd) are compared with the spectra of metallic Pr and Nd. (b) 3d5/2 and 3d3/2 electron states of Pr and Nd in PrPdSb and NdPdSb and (c) Auger PdMn45VV in PrPdSb and NdPdSb compounds and pure Pd.](image)

In the next step the Pr and Nd 3d XPS spectra of the RPdSb (R= Pr, Nd) compounds are analysed (see Fig. 2b). The spin-orbit splitting dominates the spectral structure of the 3d XPS peaks. At the low-binding-energy side of the 3d5/2 and 3d3/2 main lines of shake down satellites are observed which are known to account for the screened Pr 3d94f3 and Nd 3d94f4 final states [8]. In the PrPdSb XPS spectrum (see Fig. 2b) the peaks at 933.0 eV and 953.3 eV correspond to the 3d9/24f2 and 3d9/24f2 configurations, respectively, while those at 929.7 eV and 950.0 eV were identified as the satellites. A similar distribution of the peaks is observed in the XPS spectrum of NdPdSb. The peaks at 982.2 eV and 1005.2 eV correspond to the 3d9/24f3 and 3d9/24f3 configurations, while those at 975.2 eV and 101.9 eV are their satellites.

The separation of the peaks bases on the Doniach-Šunjic theory [9] which gives the intensity ratio \( r = \frac{I(f^{n+1})}{I(f^n) + I(f^{n+1})} \). It was possible to determine the coupling parameter \( \gamma \) using the measured intensities of the final 3d94f9 and 3d94f9 states as well as calculations of the intensity ratio \( r \) as a function of \( \gamma \) previously published. The coupling parameter \( \gamma \) is defined as \( pV^2\gamma_{\text{max}} \), where \( \gamma_{\text{max}} \) is the maximum of the density
of conduction states and V is the hybridization on the basis of the Gunnarsson-Schönhammer model [10]. A rough estimation of $\gamma$ for Pr and Nd ions seems to be possible if one assumes that for Pr and Nd the calculated intensity ratio $r$ changes with $\gamma$ the same as in the case of Ce [11].

The $r$ value of PrPdSb equal to 0.213 corresponds to the hybridization energy 110 meV. A similar calculation for NdPdSb gives $r$ equal to 0.019 and the adequate hybridization energy 9.4 meV. These results indicate that with an increase in the number of the 4f electrons the hybridization energy decreases. The large difference in the value of hybridization (coupling energy $\gamma$) equal 110 meV for PrPdSb and 9.4 meV for NdPdSb suggesting a considerable hybridization for PrPdSb. The hybridization of 4f levels in PrPdSb is a factor which leads to the reduction of the Pr magnetic moment. The Pr magnetic moment calculated on the basis of the determined electronic structure (equal 2.2 $\mu_B$) is smaller than the free Pr$^{3+}$ ion value (3.2 $\mu_B$) while the calculated values of the Nd magnetic moment in the NdPdSb compound (equal 3.14 $\mu_B$) is close to the free Nd$^{3+}$ ion value (3.27 $\mu_B$) [12].

For PrPdSb the absence of magnetic moments at the Pr sites results from a strong hybridization of the 4f electrons of Pr$^{3+}$ ions with conduction electrons. This is consistent with the large value of the electronic coefficient of the specific heat $\gamma$ equal 75 mJ/molK$^2$ [13]. The density of states $N(E_F)$ determined from the $\gamma$ value is of 3.18 states/eV spin f.u. and the values of the density of states calculated on the basis of the electronic structure data are 1.60 states/eV spin f.u. for PrPdSb and 0.73 states/eV spin f.u. for NdPdSb [12].

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