Influence of Yttrium Substitution on the Electronic Structure and Magnetic Moment of $Gd_{7-x}Y_xPd_3$ ($x = 0, 1, 2, 3, 4$)

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The electronic structure and magnetic properties of $Gd_{7-x}Y_xPd_3$ ($x = 0, 1, 2, 4$) single crystals were examined. These compounds crystallized in the same crystal structure type (Th_7Fe_3) with the same c/a ratio of 0.63. A strongly anisotropic behavior of the magnetic and transport properties was found. Magnetic frustration and spin fluctuations on the palladium atoms are responsible for the complex magnetic properties of this ternary compound. As a part of current research we presented further characteristic of the $Gd_{7-x}Y_xPd_3$ ($x = 0, 1, 2, 4$) single crystal.

1. Introduction

Magnetic refrigeration has been recognized as being an alternative technology to the conventional vapor-compression one [1]. Recently the $Gd_5(Ge_{1-x}Si_x)_4$ alloys were widely investigated [1]. Due to the discovery of the giant magnetocaloric effect (MCE) in the $Gd_5(Ge_{1-x}Si_x)_4$, drive to identify materials with near room temperature magnetocaloric properties increased. Within a few years several other families of materials have been found to exhibit the large MCEs near ambient temperatures. These include e.g. RM_2 (M = Al, Co, Ni), $MnFe(P_{1-x}As_x)$, $Mn(As_{1-x}Sb_x)$ and $La(Fe_{13-x}Si_x)$ were reported [1, 2]. Canepa et al. [3] found the magnetocaloric effect for polycrystalline Gd_7Pd_3 and ferromagnetic transition determined at $T_C = 323$ K. The magnetic properties and temperature dependences of the lattice parameters of Gd_7T_3 (T = Rh and Pd) and $Gd_{7-x}Y_xPd_3$ ($x = 1, 2, 4$) single crystals have already been reported [4–8]. These compounds crystallized in the same crystal structure type (Th_7Fe_3) with the same c/a ratio of 0.63. A strongly anisotropic behavior of the magnetic and transport properties was observed. Moreover, there is a large difference between the values of the ordering temperatures between Gd_7Pd_3 and Gd_7Rh_3. The Gd_7Pd_3 orders ferromagnetically at 334 K while Gd_7Rh_3 displays antiferromagnetic transition at 140 K. The nonmagnetic yttrium substitution into the gadolinium sublattice in the $Gd_{7-x}Y_xPd_3$ series influences the mag-

netic properties and decreases the ordering temperature without changing the crystal structure of the compounds [6]. The Gd_7Pd_3 exhibits ferromagnetic transition at 334 K, Gd_6YPd_3 orders at 299 K, $Gd_5Y_2Pd_3$ at 255 K, $Gd_4Y_3Pd_3$ at 235 K while $Gd_3Y_4Pd_3$ displays transition at 197 K. The Gd sublattice in the unit cell of the examined compounds has a large and localized magnetic moment. Thus the exchange interactions between Gd ions have here a dominating mechanism being responsible for the formation of a magnetic ordering. It is realized by the Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions via the conduction electrons. The substitution of one yttrium atom modifies the valence band and influences the magnetic properties [6]. The aim of this work is to examine the influence of the yttrium for gadolinium substitution on the electronic structure and magnetic moment of $Gd_{7-x}Y_xPd_3$.

2. Experimental details

Single crystals of $Gd_{7-x}Y_xPd_3$ ($x = 0, 1, 2, 3, 4$) were obtained by the Czochralski method from a levitated melt using high purity starting materials. The X-ray photoelectron spectra (XPS) of the above single crystal were measured with monochromatized Al K_α radiation (1486.6 eV) at room temperature using a PHI 5700 ESCA spectrometer. The energy spectra of the electrons were determined by a hemispherical mirror analyzer with an energy resolution of about 0.3 eV. Magne-

tization was measured using a Quantum Design MPMS-XL-7AC SQUID magnetometer in the temperature range 1.9–300 K in applied magnetic fields up to 7 T.

3. Results and discussion

The XPS spectra obtained for the monocrystalline samples $Gd_{7-x}Y_xPd_3$ ($x = 0, 1, 2, 3, 4$) show no contaminations with carbon and oxygen. All the single crystals were broken under UHV conditions and measured in a wide energy range. XPS spectrum of the $Gd_4Y_3Pd_3$ single crystal in the energy range 0–1400 eV, as an example, is shown in Fig. 1. Moreover, using the XPS spectra the stoichiometry was checked. It was in agreement with the nominal one and stable in different crystal fragments.
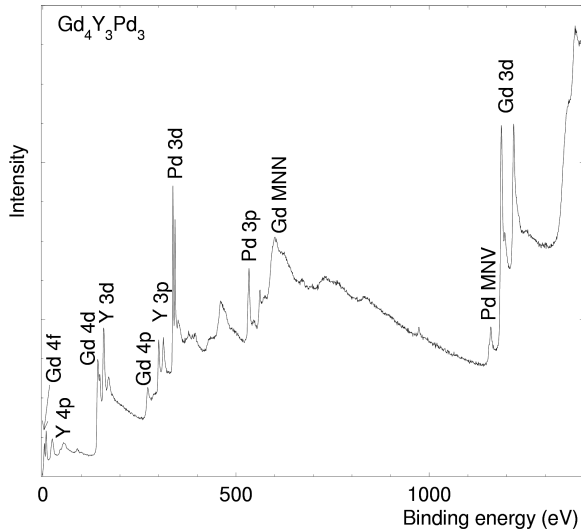

Fig. 1. XPS spectrum of a $Gd_4Y_3Pd_3$ single crystal in the energy range 0–1400 eV.

The measured XPS valence band of Gd_7Pd_3 is compared with Gd_6YPd_3, $Gd_5Y_2Pd_3$, $Gd_4Y_3Pd_3$ and $Gd_3Y_4Pd_3$ (Fig. 2). The Pd 4d states are narrowing and moving away from the Fermi level to higher binding energy (full width at half maximum $\Gamma_{FWHM} = 1.4$ eV, binding energy BE = 3.7 eV) in comparison with elemental Pd ($\Gamma_{FWHM} = 4.1$ eV, BE = 0.95 eV). Such behaviour for all compounds is observed. It is due to a reduction of overlap of the Pd 4d orbitals of the neighboring Pd atoms in the compound. The Pd 4d states together with Y 4d are well separated from the Gd 5d ones. The Gd 5d states form a shoulder at the Fermi level. The 5d band of gadolinium is almost empty and has a tendency to take up d electrons, while the almost full d-band of palladium can only lose them. For $Gd_5Y_2Pd_3$ the biggest narrowing of the Gd 5d states at the Fermi level is observed. The hybridization process may lead to spin fluctuations on the palladium and seems to increase the density of states at the Fermi level. For the $Gd_4Y_3Pd_3$ and $Gd_3Y_4Pd_3$ the Gd 5d states are similar. Due to a difference in time window for spin fluctuations (10^{-13} s)
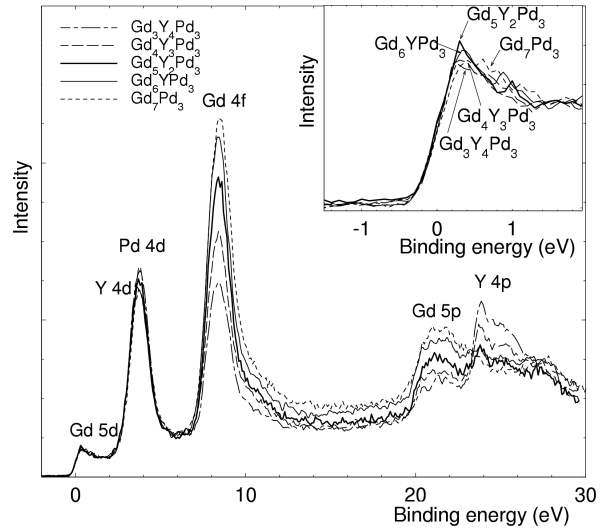

Fig. 2. XPS valence band of the Gd_7Pd_3, Gd_6YPd_3, $Gd_5Y_2Pd_3$, $Gd_4Y_3Pd_3$ and $Gd_3Y_4Pd_3$ compounds with the Gd 4f, Gd 5p and Y 4p states (inset shows the Gd 5d states).
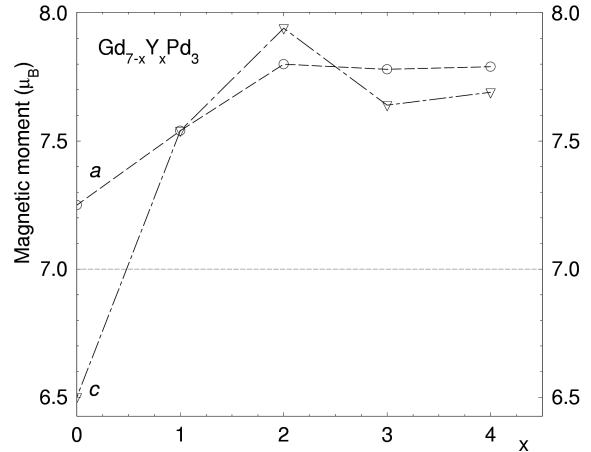

Fig. 3. Change of the magnetic moment along the principal crystallographic directions of the Gd_7Pd_3, Gd_6YPd_3, $Gd_5Y_2Pd_3$, $Gd_4Y_3Pd_3$ and $Gd_3Y_4Pd_3$ compounds with the Gd 4f, Gd 5p, and Y 4p states.

and photoelectron process (10^{-16} s), the peak at Fermi level may be observed. Moreover, the substitutions of yttrium into gadolinium sublattice cause decrease in the Gd 4f line and increase in Y 4d line intensities.

The magnetization measurements results of $Gd_{7-x}Y_xPd_3$ are in agreement with the electronic structure changes. The saturation moment value calculated per gadolinium atom for both the directions measured for $Gd_{7-x}Y_xPd_3$ is shown in Fig. 3. The values of the saturation magnetic moment are higher than the value 7 μ_B expected if only the Gd atoms would carry a magnetic moment. This enhancement indicates that also the Pd atoms carry a magnetic moment in

the $Gd_{7-x}Y_xPd_3$ compounds. The saturation moment value for Gd_7Pd_3 along the a axis was 7.25 μ_B and 6.5 μ_B [5, 6] along the c axis, for Gd_6YPd_3 the moment of 7.54 μ_B for both the measured directions was found [6]. In the case of $Gd_5Y_2Pd_3$ the magnetization for both the axes attains practically the same value of 7.9 μ_B [8]. In $Gd_4Y_3Pd_3$ magnetic moment was found to be 7.78 μ_B for a axis and 7.64 μ_B for c axis and in $Gd_3Y_4Pd_3$ the moment of 7.79 μ_B was found for a axis and 7.69 μ_B for c axis. A comparison of magnetic moments values ensue that the substitution of the Gd atoms by the Y atoms changes substantially magnetic behaviour of the $Gd_{7-x}Y_xPd_3$ alloys. The enhancement of the saturation magnetic moment may be related to an itinerant electron contribution associated with $4d$ of the Pd ions and with $5d$ of the Gd ions. The contribution of $4d$ and $5d$ bands is documented by XPS data shown above, where these bands are located near the Fermi level. We must point out that the highest enhancement of magnetic moment for $Gd_5Y_2Pd_3$ is observed and for this compound exhibits also the biggest narrowing of the Gd $5d$ states at the Fermi level.

4. Summary

The exchange interactions between Gd ions have here a dominating mechanism being responsible for the formation of a magnetic ordering. It is realized by the RKKY interactions via the conduction electrons. The substitution of one yttrium atom modifies the valence band and influences the magnetic properties. The enhancement of the saturation magnetic moment may be related to palladium sublattice. Recently the Compton scattering research of Gd_7Pd_3 confirmed the existence of magnetic moment on palladium atoms [9]. Thus the spin fluctuations originating from the palladium atoms due to overlapping a top of Pd $4d$ with a bottom Gd $5d$ may be responsible for the magnetic behavior of the above studied compounds. The substitution of non-magnetic yttrium into gadolinium sublattice does not cause the change in the crystal structure but changes the electronic structure which reflects in the increasing value of the Pd moment.

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