Investigation of physical properties of the Ce$_{1-x}$Pr$_x$CoGe$_3$ system

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Abstract

We present the results of our studies of physical properties for the novel Ce$_{1-x}$Pr$_x$CoGe$_3$ system performed with a number of experimental methods: magnetic susceptibility, specific heat, electrical resistivity, magnetoresistance and thermoelectric power. All investigated materials of the Ce$_{1-x}$Pr$_x$CoGe$_3$ series crystallize in the tetragonal BaNiSn$_3$-type structure. The lattice parameters and unit cell volume decreases with increasing $x$. On the basis of the measurements taken, a tentative magnetic phase diagram was created. A continuous suppresion of the long-range magnetic order was observed as the concentration of Pr increase. The critical Pr concentration was determined from linear extrapolation to the lowest temperatures ($T = 0$ K) and is equal to $x = 0.66$.

Keywords: Intermetallics, Heavy fermions, Physical properties, RKKY interaction, Kondo interaction, Magnetism

1. Introduction

Most of the interesting properties of the strongly correlated systems are based on the $f$ electrons. Extensive experimental and theoretical efforts focus on unconventional superconductivity and effects, like the heavy fermion state, deviations from the Fermi liquid behaviour, and competition between the magnetic RKKY interaction and Kondo effect \[4\]. Some of these physical effects are observed under special conditions, which can be steered by the control parameter $\delta$ corresponding to the quantity $|JN_F|$, where $J$ is exchange integral and $N_F$ is the conduction band density of states at the Fermi level $E_F$ \[7\]. In most cases $\delta$ is changed by applying an external magnetic field, hydrostatic pressure or by chemical substitution.

Non-centrosymmetric structures attract scientific interest as the lack of inversion symmetry is the key reason of unconventional superconductivity. One of the widely studied crystal structures is that of BaNiSn$_3$-type (space group $I4mm$, no. 107). Most of the compounds crystallizing in this structure are compossited as CeTX$_3$, where $T$-transition metal and $X$-Si, Ge or Al. The examples are: CeRhSi$_3$ \[5\], CeIrSi$_3$ \[10\], CeRhGe$_3$ \[11\], CeIrGe$_3$ \[12\], CeCuAl$_3$ \[13\] or CeAuAl$_3$ \[14\]. However, in this group of stiechiometry there are also other types of crystal structures, for example: hexagonal BaNiO$_2$-type with representative of CeCrGe$_3$ \[15\][19], CeTiGe$_3$ \[22\] or CeVGe$_3$ \[23\], or orthorhombic SmNiGe$_3$-type for CeNiGe$_3$ \[26\]. One of most interesting compounds from this group is CeCoGe$_3$, with three magnetic phase transitions at $T_{N1} = 21$ K, $T_{N2} = 12$ K and $T_{N3} = 8$ K \[28\][32]. It also reveals superconductivity under pressure \[33\][34] and exhibits a quantum critical point after substitution of Ge with Si \[35\][37]. Even more complicated magnetism occurs in the system CeCo$_{1-x}$Fe$_x$Ge$_3$ \[38\][40]. In addition, there are several other magnetic compounds based on the stiechiometry RECoGe$_3$ ($RE$—rare earth), for example, EuCoGe$_3$ \[41\] or NdCoGe$_3$ \[42\]. The only exception is PrCoGe$_3$ - a paramagnetic compound with low values of the electronic specific heat coefficient $\gamma$ parameter indicating metallic state \[45\]. The previous investigation of the PrCoGe$_3$ Fermi surface revealed that in this compound praseodymium behaves identically to lanthanum, as there is no contribution of $f$ electrons to the Fermi surface \[46\]. However, justification for this state has not been provided.

The aim of this article was to study an effect of substitution on physical properties of the Ce$_{1-x}$Pr$_x$CoGe$_3$ system and to identify the role of the rare earth element in the magnetism of these alloys. The evolution of magnetism is different than in the previously studied CeCo$_{1-x}$Fe$_x$Ge$_3$ system. The energy of RKKY interaction, which is responsible for the magnetic ordering, does not decrease directly as magnetism is rather disturbed as the Pr ions replacing the Ce ions do not contribute to magnetic ordering and they distract the interactions between Ce ions. A similar situation applies to the Kondo interaction, since the Kondo contamination effect occurs for a sample of $x = 0.8$ and the PrCoGe$_3$ parent compound exhibits metallic behavior. This is the evidence of a weakening of the Kondo interaction strength with an increase of $x$. It also means that there is a Pr concentration threshold, in which magnetism and Kondo lattice are no longer collective in the sample volume. Extensive experimental methods also enabled the explanation of the Pr behaviour in the studied alloys and...
the estimation of the influence of the crystal electric field (CEF) on the properties of the Ce$_{1-x}$Pr$_x$CoGe$_3$ series.

2. Methods

2.1. Experimental

The polycrystalline samples were obtained by melting high purity elements several times in an arc furnace to ensure the sample homogeneity. Final mass loss was less than 1%. Finally, the samples ingots were wrapped in tantalum foil, encapsulated in evacuated quartz tubes, and annealed at 900°C for 7 days.

The crystal structure of prepared samples was investigated with X-ray diffraction measurements performed on X’pert Pro PANalytical device with Cu-Kα radiation source in room temperature. To test the physical properties of the Ce$_{1-x}$Pr$_x$CoGe$_3$ system, a number of experimental methods were used. As the main measuring device we used a Quantum Design Physical Property Measurement System (QD PPMS) with appropriate options for specific measurements. Firstly, the zero field cooling (ZFC) and field cooling (FC) curves of magnetic susceptibility were measured with a vibrating sample magnetometer (VSM) and measurements were performed in ultrahigh vacuum chamber (UHV) with base pressure of 10$^{-10}$ Torr. The resistivity measurements were performed without an applied magnetic field in the range of 2 – 300 K, while magnetoresistance was measured at magnetic field values up to 9 T for temperatures 2 – 30 K. Thermoelectric power data were collected using four probe method of the thermal transport option (TTO) in the temperature range 2 – 300 K. Finally, the X-ray photoelectron spectroscopy (XPS) measurements were performed with the use of PHI 5700/660 Physical Electronics spectrometer. The spectra were analyzed at room temperature using monochromatized Al Kα radiation (1486.6 eV). The clean surface of samples was obtained by in-situ fracturing. All procedures and measurements were preformed in ultrahigh vacuum chamber (UHV) with base pressure of 10$^{-10}$ Torr.

2.2. Calculations

The density functional theory (DFT) calculations of the CeCoGe$_3$, Ce$_{0.5}$Pr$_{0.5}$CoGe$_3$ and PrCoGe$_3$ compositions were carried out using the full-potential local-orbital scheme (FPLO) [45]. We used the experimental lattice parameters $H_6$ [47] and atomic positions [28] $H_6$, see Table 1 and fig. 1. CeCoGe$_3$ and PrCoGe$_3$ crystallize in a tetragonal non-centrosymmetric structure of the BaNiSn$_3$-type, space group $I4mm$ [28] [46] [47]. The considered intermediate composition Ce$_{0.5}$Pr$_{0.5}$CoGe$_3$ was modeled as an ordered compound with one Ce and one Pr atom per unit cell (two formula units), see fig. 1(b). To visualize crystal structures we used the VESTA code [49]. The calculations were performed in a full-relativistic mode within the generalized-gradient approximation (GGA) for exchange-correlation potential in the form of Perdew-Burke-Ernzerhof (PBE) [50] with the FPLO18.00-52 version of the code. We used k-meshes equal to $20 \times 20 \times 20$ and energy convergence criteria equal to 2.72×10$^{-6}$ eV (10$^{-7}$ Hartree). For Ce-based compounds with an open Ce 4f shell, it is important to improve the description of local spin density approximation (LSDA) by using e.g. the LSDA + U interaction term (LSDA+U). LSDA + U adds Hubbard U intra-atomic repulsion term in energy functional and can significantly improve the LSDA results. A detailed overview of the LSDA+U methods is provided, for example, in the article Ylvisaker et al. [51].

For the compositions in question, we used the fully localized limit (PLL) of LSDA+U functional introduced by Czyżyk and Sawatzky [52], sometimes referred also as the atomic limit (AL). The Hubbard U repulsion term introduced in Ce 4f and Pr 4f orbitals was equal 6 eV. This value was calculated previously for Ce [53]. We have also checked that the effect of the on-site repulsion U on the Co 3d orbitals is weak, so the U$_{3d}$ corrections can be neglected in that case. A similar first-principles approach has been taken to PrO$_2$ [54] and other lanthanides systems with

| composition         | a (Å) | c (Å) | Ref.   |
|---------------------|-------|-------|--------|
| CeCoGe$_3$          | 4.32  | 9.835 | [47]   |
| PrCoGe$_3$          | 4.308 | 9.829 | [46]   |
| Ce$_{0.5}$Pr$_{0.5}$CoGe$_3$ | 4.314 | 9.832 | interpolated |

Table 1: Lattice parameters of Ce$_{1-x}$Pr$_x$CoGe$_3$ compounds.

Figure 1: The crystal structure models of (a) PrCoGe$_3$ and (b) Ce$_{0.5}$Pr$_{0.5}$CoGe$_3$ compositions. They crystallize in a tetragonal non-centrosymmetrical structure of the BaNiSn$_3$-type, space group $I4mm$ [28] [46] [47].
general formula LnO$_{1-x}$F$_2$BiS$_2$, where Ln = La, Ce, Pr, and Nd [55]. A similar analysis for isostructural system CeCo$_{0.5}$Fe$_{0.5}$Ge$_3$ have been presented by us [40].

The valence band X-ray photoelectron spectra were calculated based on the band-structure results. The densities of states (DOS) of individual orbitals have been convoluted by the Gaussian function with a full width at half maxima parameter $\delta$ equal to 0.3 eV. The aim of convolution was to imitate the experimental broadening resulting from the apparatus resolution, lifetime of the hole states and thermal effects. Subsequently, the partial densities of states were multiplied by the appropriate photoionization cross-sections [56].

3. Results and discussion

3.1. Crystal structure

The crystal structure of the prepared samples was examined by X-ray diffraction (XRD) measurements at room temperature. The results were analyzed using the FULLPROF [57] program (an exemplary refinement is shown in figure 2) and it revealed that all samples have the desired single-phase non-centrosymmetric tetragonal BaNiSn$_3$-type structure. The crystal lattice parameters are presented in figure 3. Values of the parameters $a$ and $c$ and the volume $V$ decrease with the addition of Pr, as the Pr ion has smaller radius than Ce ion. The ratio $c/a$ presents small growth of values with the increase of Pr content, suggesting an elongation of the elemental cell.

3.2. Magnetic properties

Figure 4 presents temperature dependences of the magnetic susceptibility measured at low temperatures. In part (a) of figure 4 the sample with $x = 0.2$ is shown. Similarly as we have done for the series CeCo$_{1-x}$Fe$_x$Ge$_3$ [58], here we denoted the temperatures of phase transitions as $T_i$ ($i = 1, 2, 3$), as the character of the magnetic ordering may change depending on the range of substitution. The first magnetic transition is shifted to $T_2 = 12$ K, while $T_2$ to 8 K and $T_3$ to 5 K. As for the CeCo$_{1-x}$Fe$_x$Ge$_3$ system, a small amount of substituted element results in the appearance of the ferromagnetic part in the transitions at $T_2$. However, a metamagnetic transition is still visible in figure 5 for the magnetization curve of the sample with $x = 0.4$. This may suggest that magnetic structure is more or less preserved with the change to ferrimagnetic ordering instead of antiferromagnetic one. This change might be caused by a small difference in cell parameters, which changes the RKKY interaction into a ferromagnetic type or by magnetic disorder, which has a noticeable contribution visible by the large discrepancy between the ZFC and FC curves. In this case, we can assume that the Ce valence is 3, adding 5$d^6$s$^2$ electrons (neutral electron configuration of Ce is [Xe]4f$^1$5d$^5$s$^2$) to the conduction band and with one 4f$^1$ electron entangled to the ion, while the Pr$^{3+}$ ion has [Xe]4f$^2$ configuration state giving 4f$^1$6s$^2$ electrons (neutral electron configuration of Pr is [Xe]4f$^3$6s$^2$), resulting in an unchanged number of electrons in the conduction band and thus directly not modifying the RKKY and...
measurements and we calculated the magnetic entropy change. We used magnetocaloric effect (MCE) isotherms measured temperatures of phase transitions without CEF contribution. In order to determine CEF contribution, we assumed that the cobalt contribution is negligible, the magnetic susceptibility results might be inaccurate, because of strong overlapping of the Curie-Weiss law fitted with the Curie-Weiss law of phase transition, whereas the next one is at $T_2 = 3$ K. A broad peak around 12 K is associated with CEF of praseodymium, it is also visible for other samples with $x ≥ 0.6$. The splitting between ZFC and FC curves also suggests a high disorder in the magnetic structure. In figure 5 there is a small hysteresis with no metamagnetic transition in the measured range of the magnetic field, differently than for the sample with $x = 0.2$.

The sample with $x = 0.6$ also exhibits splitting between ZFC and FC curves. A small hump at $T = 2$ K implies a possibility of phase transition. Additionally, for this sample the hysteresis is not visible in figure 5. The parent compound PrCoGe$_3$ shows paramagnetic behaviour with noticeable contribution of CEF, which has been also detected for single crystal case in [100] direction [45].

The denoted temperatures of magnetic phase transitions with usage of magnetic susceptibility results might be inaccurate, because of strong overlapping of the praseodymium CEF contribution. In order to determine temperatures of phase transitions without CEF contribution we used magnetocaloric effect (MCE) isotherms measurements and we calculated the magnetic entropy change with formula:

$$ΔS_M ≈ \frac{μ_0}{ΔT} \left[ \int_0^{H_{max}} M(T + ΔT, H) dH - \int_0^{H_{max}} M(T, H) dH \right].$$

Observe a maximum and minimum can designate dominating magnetic ordering [58, 59]. The results of $ΔS_M$ in function of temperature for samples with concentrations of $x = 0.2$ and 0.4 are presented in figure 4. The sample with $x = 0.2$ shows metamagnetic transition at temperature 14.5 K as a maximum for magnetic field value of 9 T. Referring to the magnetic susceptibility results a wide peak is visible at 12 K. Considering similar situation described for CeCoGe$_3$ [58], the temperature for $T_1$ transition corresponds to metamagnetic transition resulting in $T_1 = 14.5$ K. Small hump at temperature 6.5 K and small minimum at 4 K might correspond to temperatures of phase transitions $T_2$ and $T_3$ denoted from magnetic susceptibility curves. The all three phase transitions are the same type as CeCoGe$_3$ [58]. For sample with $x = 0.4$ there is also maximum with metamagnetic transition at $T_1 = 8.5$ K, which is corresponding to the observed anomaly in the magnetic susceptibility. A wide peak indicates $T_2 = 4.5$ K.

Arrott plots for samples with concentration $x = 0.2$ and 0.4 are presented in figure 7. For both samples there is a negative curvature below temperatures $T_1$. This suggests a first order metamagnetic transition according to Banerjee criterion [60].

The Curie-Weiss law allowed to determine the valency of Pr in the Ce$_{1−x}$Pr$_x$CoGe$_3$ series. If we assume that the cobalt contribution is negligible, the magnetic susceptibility is a sum of the Ce and Pr contributions with appropriate proportions depending on the stoichiometry.
Figure 6: Calculated magnetic entropy change $\Delta S_M$ in function of temperature $T$ for $x = 0.2$ (a) and 0.4 (b). The vertical lines indicates the detected phase transitions and anomalies.

Table 2: Data obtained from fitting Curie-Weiss law using the formula: $\chi(T) = \frac{N \mu_{eff}^2}{4\pi k_B (T - \theta_p)} + \chi_0$, where $\mu_{eff}^2 = x \mu_{Pr}^2 + (1-x) \mu_{Ce}^2$. Considering previous reports, the cerium effective moment was fixed at $\mu_{Ce} = 2.54 \mu_B$. $\chi_0$ values do not evolve systematically with the increased content of $Pr$.

| $x$ (Pr) | $\mu_{eff} (\mu_B)$ | $\theta_p$ (K) | $\mu_{Pr} (\mu_B)$ |
|----------|----------------------|----------------|---------------------|
| 0        | 2.542(2)             | -63.7(2)       | -                   |
| 0.2      | 2.757(7)             | -36.6(6)       | 3.493(7)            |
| 0.4      | 3.035(13)            | -24.8(7)       | 3.653(13)           |
| 0.6      | 3.115(6)             | -16.2(3)       | 3.445(6)            |
| 0.8      | 3.345(13)            | -7.7(4)        | 3.517(13)           |
| 1.0      | 3.519(9)             | -10.3(4)       | 3.519(9)            |

Figure 7: Arrott plots for samples with concentration $x = 0.2$ (a) and 0.4 (b).

of a particular sample. To calculate the magnetic moment of praseodymium $\mu_{Pr}$, we used the formula \[ \mu_{eff}^2 = x \mu_{Pr}^2 + (1-x) \mu_{Ce}^2 \] with assumption of value of free cerium $3+$ ion $\mu_{Ce} = 2.54 \mu_B$, as it has been reported previously that in this crystal structure Ce has a magnetic moment value close to 2.50 $\mu_B$. The data resulting from the fitting of the Curie-Weiss law are presented in Table 1. For all samples, the Pr part of effective moment is around 3.50 $\mu_B$, which is close to the Pr$^{3+}$ ion. The paramagnetic Curie temperature $\theta_p$ shows a tendency to decrease with increasing $x$. This also indicates a reduction in magnetism and strength of Kondo interaction, which finally leads to paramagnetic and metallic type of behaviour for the parent compound PrCoGe$_3$.

3.3. Specific heat

Temperature dependences of the specific heat in the temperature range 1.9 – 40 K for exemplary samples and different values of the applied magnetic field are presented.
in figure[3] Values of specific heat for all samples are close to Dulong-Petit limit. The increase in magnetic field values for samples with $x = 0.2$, 0.4 and 0.6 shifts the main peaks connected with the magnetic phase transition $T_1$ towards lower temperatures, which suggests ferrimagnetic or antiferromagnetic type of ordering. If we consider the results of magnetic susceptibility and isothermal magnetization measurements, we can assume that for these samples the ferrimagnetic ordering scenario is more probable.

The sample with $x = 0.4$ presents the suppression of the main phase transition $T_1$ with the increase of the magnetic field values. For the sample with $x = 0.6$ the transition peak is around 2 K, which is visible owing to the influence of magnetic field on the curves. PrCoGe$_3$ provides results similar to those reported earlier [15], with no noticeable changes with the increase of the magnetic field. For all three samples the CEF contribution connected with praseodymium is visible as a wide peak appearing in the temperature range of 10–30 K. In addition, the increase in Pr concentration leads to the distinction of the CEF part. Due to the CEF peak, as well as the magnetic contribution below 12 K, it is difficult to determine the $\gamma$ parameter values because the correct temperature range cannot be chosen for applying the formula $C_p/T = \gamma + \beta T^2$. However, we can observe the trend of the $\gamma$ values at 2 K. For samples with $x = 0.2$ and 0.4 ($x = 0.6$ has a phase transition at $T = 2.2$ K and cannot be considered in the analysis) it can be observed that higher Pr content results in higher $\gamma$ values, which is rather related to the increase in disorder than to the enhancement of the effective mass and creation of the heavy Fermion state.

3.4. Resistivity

The results of the measurments of the temperature dependence of resistivity in the range of 2–300 K are shown in figure[9] With increasing concentration of Pr we can observe a clear reduction of the CEF contribution of cerium (broad peak around 100 K) in favor of the praseodymium CEF contribution (around 30 K). This is especially important as we can assume that there are two separate CEF contributions, which are modified by the stoichiometry of the alloy. It is necessary to consider this information in further investigation of the CEF levels for particular alloys of the system Ce$_{1-x}$Pr$_x$CoGe$_3$.

In figure[9] one can also notice phase transitions for samples with $x = 0.2$, 0.4 and 0.6 at $T_1 = 12$ K, 7 and 2 K, respectively. For sample with $x = 0.8$ there is an upturn in the lowest temperatures, which might be connected with a single ion Kondo effect. This is expected as the concentration of Ce is significantly reduced. The threshold between the Kondo lattice and the Kondo impurity effect is between a concentration of 0.6 $< x <$ 0.8, where also the magnetism is suppressed to 0 K.

Similarly as for specific heat results, where CEF contribution of praseodymium and magnetism in the lowest temperatures prevented the systematic calculation of the $\gamma$ parameter values, the same issues for resistivity do not allow to extract the $\rho_0$ parameter values. However, we can observe some tendencies, which can provide some rough conclusions. It is noticeable that the overall $\rho$ values for
alloys at the lowest temperatures increase with the addition of Pr, suggesting a growing chemical disorder (with the exception of the sample with $x = 0.8$ - it cannot be considered in the analysis as it presents the Kondo impurity effect). For the parent compound PrCoGe$_3$, we observe a metallic type behaviour with a significant CEF contribution in the temperature range of 10 – 30 K. Additionally, the parameter $RRR = 81$ has rather a high value for a polycrystalline sample. Due to the noticeable disorder visible in the entire substitution range of $x$ (excluding parent compounds).

3.5. Magnetoresistance

To improve the characterization of the magnetic properties of the studied alloys, we have carried out measurements of the resistivity as a function of the magnetic field. In figure 10a we show magnetoresistance plotted as $MR = [\rho(H, T) - \rho(0, T)]/\rho(0, T)$ for the sample with $x = 0.2$. There is a metamagnetic transition reflected as a change from positive to negative values of $MR$ at temperatures below 12 K and at magnetic field of about 5 T, which confirms that the magnetic structure of CoCoGe$_3$ is still maintained for sample with $x = 0.2$. Similar behaviour can be observed for the sample with $x = 0.4$, but the metamagnetic peak is in the region of negative $MR$ values, which may suggest a ferrimagnetic ordering with a larger ferromagnetic contribution than in the case of $x = 0.2$. For higher temperatures, above 18 K for $x = 0.2$, magnetoresistance reveals a wide positive peak, which can be interpreted as the effect of CEF. This is also visible at lower temperatures for samples with $x = 0.4$ and 0.6. Although the CEF contribution increases with the content of praseodymium, it does not overlap with the magnetic part as the magnetic transitions occur at lower temperatures than the CEF effects. Further increase of temperature causes disappearance of the peak, because we are moving out from the CEF region. A linear, metallic-type form of the positive $MR$ is revealed.

A more complicated situation is presented in figure 10b, where the parent compound PrCoGe$_3$ presents a typical metallic-type $MR$, but with high values up to 250%. As metallic behaviour is expected, the source of high $MR$ values might be not as clear. At first glance, this may be related to the $MR$ formula and low values of $\rho_0$. Looking at the results of other samples and the contribution of the CEF part to $MR$, this contribution is not evident in the case of PrCoGe$_3$. Instead, the CEF part is covered by a metallic contribution, unlike for sample with $x = 0.2$, where the magnetic contribution is taking this role. Previously, the explanation of the giant MR in Tb$_2$Ni$_2$Si$_3$ and Sm$_2$Ni$_3$Si$_3$ has been connected with the layered magnetic structure. Additionally, for PrNiGe$_3$ compound, the authors have suggested the influence of the magnetic field on the mobility of conduction electrons and magnetic ordering. Since the high values of $MR$ in intermetallic compounds are still not fully explained, we suggest that in our case the interpretation related to the modification of electron mobility might be possible. For LaCoGe$_3$ the results of $MR$ are similar to the results PrCoGe$_3$. This is expected because Pr behaves as La in these compounds, providing similar influence on the band structure, as it has been reported by Kawai, et al. [10]. This may be an indication that the giant $MR$ for PrCoGe$_3$ compound is associated with the band structure and the mentioned modification of the mobility of the conduction electrons.

3.6. Seebeck coefficient

In figure 11, the values of the Seebeck coefficient as a function of temperature are presented. A wide peak around 100 K is observed for all samples containing cerium, which is connected with the cerium CEF contribution. The highest value $S = 43.4(2) \, \mu V/K$ is denoted for sample $x = 0.2$ at temperature of 95 K. The decrease in maximum values is associated with the decreasing Ce content, whereas the praseodymium CEF contribution visible in range of 10 – 30 K becomes more pronounced with increasing Pr content in alloys. For PrCoGe$_3$ very low $S$ values are observed. However, if we consider the formula $S = AT + BT^3$, the linear character of the curve suggests the dominance of the electron diffusion part with almost no contribution of the phonon drag part.
Figure 11: Temperature dependence of the Seebeck coefficient of the Ce$_{1-x}$Pr$_x$CoGe$_3$ samples, plotted in two different representations: (a) $S$ vs $T$ and (b) $S/T$ vs log$T$.

Figure 12: XPS survey spectrum of Ce$_{1-x}$Pr$_x$CoGe$_3$ series for selected samples with $x = 0.8$ and 0.4.

Figure 13: XPS spectra for selected samples from Ce$_{1-x}$Pr$_x$CoGe$_3$ series with $x = 0.1$ to 0.9.

Figure 14(a): XPS spectra for selected samples from Ce$_{1-x}$Pr$_x$CoGe$_3$ series with $x = 0.1$ to 0.9.

Figure 14(b): XPS spectra for selected samples from Ce$_{1-x}$Pr$_x$CoGe$_3$ series with $x = 0.1$ to 0.9.

3.7. X-Ray photoelectron spectroscopy

Exemplary X-ray photoelectron spectra of Ce$_{1-x}$Pr$_x$CoGe$_3$ alloys collected in a wide binding energy range up to 1350 eV with the identification of core levels and Auger lines are shown in figure 12. For all sample we observed low content of oxygen and carbon, suggesting good quality of the samples received.

For all studied samples the XPS valence bands (VBs) in the energy range $0 - 12$ eV are presented in figure 13. In this BE range we observed three broad structures. The broad peak closest to the Fermi level ($E_F = 0$ eV) is formed by the Pr, Ce ($5d$, $6s$), Co $3d$, Ge $4p$ and Ce $4f^1$ states. The source of the middle peak ($\sim 4.0$ eV) is mainly due to the Pr $4f$ and Ce $4f^0$ states. Therefore, the position and relative intensity of this peak changes with the change of Ce/Pr concentration. The last structure, broad band of small intensity near 8.0 eV, origin from Ge $4s$ states. The broadening of all of those peaks is related to the hybridization of conducting electrons and $4f$ electrons.

In BE region from 90 to 140 eV (figure 14(a)) we observed three sets of spin-orbit splited peaks related to Ce $4d$, Pr $4d$, and Ge $3p$ states. The positions of the peaks are in good agreement with the ones published for similar systems [67, 69]. Additionally, a broad peak assigned to Ce $3s$ state is present at 101.0(1) eV. Due to the overlapping of the Ce $4d$ spectrum with the Pr $4d$ and Ge $2p$ states, nothing can be said about a possible mixed valence of the Ce states. While the relative intensity of the peaks associated with Ge is constant for all samples, the intensity of the peaks associated with Pr and Ce varies significantly for different samples.

The Co $2p$ XPS spectra for selected samples from Ce$_{1-x}$Pr$_x$CoGe$_3$ series are shown in figure 14(b). The position of the Co $2p_{3/2}$ and $2p_{1/2}$ core levels in all investigated samples is around 778.3(1) and 793.4(1) eV, respectively. The Co $2p_{3/2} - 2p_{1/2}$ spin-orbit splitting is about 15.1 eV. The resulting values are practically the same as for pure metallic Co [70]. The lack of additional satellite peaks suggests that there are no Co oxides and that the charge transfer can be neglected in this system. Therefore, the oxidation state of a Co in the Ce$_{1-x}$Pr$_x$CoGe$_3$ series is zero (0). Ge shows a strong peak
The presence of $4f$ elements in the system under consideration motivates us to go beyond LSDA formalism and apply the LSDA plus on-site repulsion term U (LSDA+U) approach. For the reason that the on-site repulsion term $U$ applied to Ce $4d$ orbitals does not affect noticeably the positions of clear peaks from the Ce $4f$ states, we observed set of two broad peaks which originates from spin-orbit splitting of 3d states. The spin-orbit splitting is equal to 18.7(1) and 20.4(1) eV for Ce and Pr, respectively. The resulting spectra for Pr look very similar to those published for pure Pr and other compounds containing Pr \[72\] \[74\]. No visible changes in the Ce an Pr 3d spectra have been observed with the change in concentration $x$. Analysis of XPS spectra for states 3d Ce and Pr can provide useful information about valence state and hybridization strength. Therefore, we used Gunnarsson-Schönhammer theory to describe these spectra \[73\] \[76\]. The exemplary analysis of the Ce 3d and Pr 3d XPS spectra are presented in figure \[15\] for Ce$_0.6$Pr$_{0.4}$CoGe$_3$ and figure \[14\] for Ce$_0.6$Pr$_{0.4}$CoGe$_3$, respectively. To model the background, the Tougaard algorithm was used \[77\]. Relative small values of the intensity ratio $r_2 = I(f^2)/[I(f^3) + I(f^2)]$, implicates weak electron hybridization. Moreover, the absence of clear peaks from the Ce $4f^0$ states clearly indicates a full occupancy of the $f$ orbital. In order to get the best possible fittings, it was necessary to include additional peaks (dotted lines in figure \[15\] and \[15\]). In case of Ce 3d states we considered two additional peaks at $\sim$ 892 eV and $\sim$ 916 eV, while for Pr 3d spectra additional peak at $\sim$ 955 eV was added. According to the literature, these additional structures may originate from different excitations, e.g. plasmon energy loss \[7\].

3.8. first-principles calculations

3.8.1. Relativistic Atomic Energies

We start the theoretical analysis by presenting the widest range of the electronic structure for the representative composition CeCoGe$_3$. figure \[17\] shows the relativistic atomic energies on three successively decreasing ranges. The middle one can be compared with the measured XPS survey spectrum presented before. The atomic energies are attributed to particular orbitals, where the scales allow for it. The calculated positions of the energy states are in a good agreement with the XPS experimental results presented before.

3.8.2. X-ray Photoelectron Spectra

The main purpose of our first-principles calculations is the interpretation of the measured XPS valence band spectra and investigations of magnetic properties. To this end, we prepare models of the most characteristic compositions CeCoGe$_3$, Ce$_0.5$Pr$_{0.5}$CoGe$_3$ and PrCoGe$_3$ and determine for them the density of states and the spectra of X-ray photoelectrons.

The presence of $4f$ elements in the system under consideration motivates us to go beyond LSDA formalism and apply the LSDA plus on-site repulsion term U (LSDA+U) approach. For the reason that the on-site repulsion term $U$ applied to Ce $4f$ orbitals does not affect noticeably the part of the valence band located below the $E_F$, in our previous work on CeCoGe$_3$ we presented only the XPS spectra
calculated without \( U \). However, because in contrast to the Ce case the on-site repulsion \( U \) applied to Pr \( 4f \) orbitals significantly affects the valence band below \( E_F \), we decide to consequently present all the calculated XPS spectra with taking into account the on-site repulsion term \( U_{4f} \) equal to 6 eV, see fig. 18. Comparison of the XPS spectra calculated for CeCoGe\(_3\), Ce\(_{0.5}\)Pr\(_{0.5}\)CoGe\(_3\) and PrCoGe\(_3\) shows that the bands between 0 and 6 eV consist mainly of Co \( 3d \) shares and a much smaller Ge \( 4p \) shares. With increasing Pr concentration the new maximum for Pr \( 4f \) is formed and develop at about 4 eV and at the same time the Ce \( 4f \) contribution observed on the Fermi level decreases. The main features of the calculated XPS spectra are in reasonable agreement with the experimental results shown before.

3.8.3. Charge Analysis

The Table 3 presents the excess electron numbers (resultant charges) calculated for CeCoGe\(_3\) and PrCoGe\(_3\) compounds, as calculated with the FPLO18 code using the PBE functional without spin polarization, treating the relativistic effects in a full 4-component formalism (including spin-orbit coupling) and taking into account an on-site repulsion term \( U_{4f} \) equal to 6 eV. The inequivalent atomic sites are considered according to Refs. [28, 46]. Unlike remaining sites, the multiplicity for Ge2 per formula unit is two instead of one.

| formula/site   | Ce/Pr | Co | Ge1 | Ge2 |
|----------------|-------|----|-----|-----|
| CeCoGe\(_3\)  | -1.23 | 0.17 | 0.47 | 0.30 |
| PrCoGe\(_3\)  | -1.16 | 0.18 | 0.43 | 0.27 |

Table 3: Excess electron number (resultant charge) for CeCoGe\(_3\) and PrCoGe\(_3\) compounds, as calculated with the FPLO18 code using the PBE functional without spin polarization, treating the relativistic effects in a full 4-component formalism (including spin-orbit coupling) and taking into account an on-site repulsion term \( U_{4f} \) equal to 6 eV. The inequivalent atomic sites are considered according to Refs. [28, 46]. Unlike remaining sites, the multiplicity for Ge2 per formula unit is two instead of one.

+0.30) sites and a similar picture is observed for PrCoGe\(_3\). Some more details about the orbital filling is provided from the Mulliken electronic population analysis [79], see Table 4. For Ce/Pr sites, we observe a slight depopulation of \( 5p \) orbitals and a low occupation of \( 6s \) and \( 6p \) orbitals. The large difference between the Ce and Pr electronic configuration is found for \( 4f \) orbitals (0.98 versus 2.15), which comes from the difference in atomic numbers of the ele-
of charge on 4p and 4d orbitals and partial depopulation of 4s orbitals, with respect to the electronic configuration of the ground state of a neutral Ge atom (3d\(^{10}\) 4s\(^2\) 4p\(^2\)). In summary, chemical bonds in CeCoGe\(_3\) and PrCoGe\(_3\) compounds result mainly from the interaction of Ce/Pr 5d, Co 3d, and Ge 4p and 4s orbitals.

### 3.8.4. Magnetic properties

Our magnetic measurements presented before confirmed the observed previously appearance of three magnetic phase transitions at 21, 12 and 8 K for CeCoGe\(_3\) \([29]\). They have been interpreted as the transitions between paramagnetic, ferrimagnetic, and antiferromagnetic configurations \([28]\). We also confirmed experimentally that the finding of lack of magnetic order in PrCoGe\(_3\) \([45]\). Furthermore, for PrCoGe\(_3\) it has been found previously that the magnetization in a magnetic field parallel to 001 direction indicates characteristic metamagnetic transition at 50 T \([45]\). Furthermore, our measurements indicated ordered magnetic ground state for Ce\(_{1-x}\)Pr\(_x\)CoGe\(_3\) system with Pr concentration \(x\) up to about 0.6.

In order to investigate the magnetic properties of
leads to an image with 4$f$ states split into 4$f_{5/2}$ and 4$f_{7/2}$. Moreover, the application of the on-site repulsion term $U$ further separates the Ce 4$f$ states into parts below and above the Fermi level. The occupied 4$f$ states form the sharp peaks at about -3 eV (Ce) and -5 eV (Pr), which indicates their localized character. The image of DOS for the intermediate composition Ce$_{0.5}$Pr$_{0.5}$CoGe$_3$ is similar to simple combination of terminal cases. The observed splitting of two spin channels is proportional to the spin magnetic moments and noticeably increases with Pr concentration.

The calculated magnetic moments are presented in Table 5. The spin magnetic moments on Ce (1.00 $\mu_B$) and Pr (2.06 $\mu_B$) are close to integers, which is related to the strong localization of occupied 4$f$ orbitals. The utilized full-relativistic approach allows us to calculate also the orbital contributions to the magnetic moments, which in case of 4$f$-electron systems are often substantial. In our case the opposite orbital magnetic moments on Ce (-0.56 $\mu_B$) and Pr (-1.42 $\mu_B$) significantly reduce the resultant total magnetic moments. Whereas, the total magnetic moment increases with Pr concentration from 0.39 $\mu_B$/formula unit for CeCoGe$_3$ up to 0.60 $\mu_B$/formula unit for PrCoGe$_3$. The magnetic moments on other elements are very small in comparison to the ones on 4$f$ elements. Moments on Co are below -0.05 $\mu_B$/atom and on Ge are below 0.02 $\mu_B$/atom.

4. Phase diagram

Based on the evolution of the phase transitions temperatures with the substitution level $x$ a magnetic phase diagram is constructed (figure 20) for the series Ce$_{1-x}$Pr$_x$CoGe$_3$. Linear extrapolation of the magnetic phase ordering temperature $T_1$ to 0 K gives a critical Pr concentration equal to $x = 0.66$. Alongside with a reduction of the magnetism, the system exhibits a decrease in
Figure 20: Magnetic phase diagram for the Ce$_{1-x}$Pr$_x$CoGe$_3$ system. Data were obtained from the results of magnetic susceptibility. Solid lines are a linear extrapolation of specific phase transitions to a temperature of 0 K. Concentrations obtained for specific phase transitions: for $T_1 - x = 0.66$, for $T_2 - x = 0.6$ and for $T_3 - x = 0.53$.

the strength of Kondo interaction. In terms of the Doniach diagram, we can assume that the system is approaching the low energy region of both interactions. This is a side opposite to the QCP region — increase in concentration $x$ directs the diagram to a region with lower values of $|J_{NF}|$, therefore any possible NFL behaviour between concentration of $x = 0.6$ and 0.8 would be connected with the formation of the Griffiths phase instead of the occurrence of the QCP. A possible explanation for the reduction of energy of both interactions may be related to the interference of both interactions due to the substitution of Pr for Ce in the crystal structure — the interactions have a specific range and placement of the Pr atom in the Ce site causes that the ranges of both interactions are too short to interact with the other nearest Ce atom. Considering that the Pr$^{3+}$ ion has two entangled $f$ electrons, the intriguing issue is also why praseodymium $f$ electrons do not interact with the valence band. Hypothetically, to explain it, these two $f$ electrons should have spin values of $\frac{3}{2}$ and $\frac{1}{2}$. This would lead to a state almost identical La$^{3+}$ with the addition of two non-interactive $f$ electrons. Moreover, this state of Pr has been indirectly confirmed by Kawai et al. [10], who has shown that the Fermi surface is identical for PrCoGe$_3$ and LaCoGe$_3$. They have also confirmed that the $f$ electrons contribute only to the cyclotron mass, which means that they are tightly entangled with the ion. A scenario with two opposing spins is possible if Hund’s rules are violated. This may occur due to a strong influence of CEF. Taking into account that the first CEF excitation is at low temperatures (visible as anomalies in all experimental results in temperature range of 10 – 30 K), this may be a reason for violation of Hund’s rules, resulting in two $f$ electrons with different spins, because the low spin state is present.

5. Conclusions

We have presented results of various physical properties for the novel Ce$_{1-x}$Pr$_x$CoGe$_3$ system, which shows the suppression of magnetic ordering with increasing $x$ in isostructural transformation. From the magnetic hysteresis and $MR$ measurements we deduced that the magnetic structure of the parent compound CeCoGe$_3$ is preserved for a low content of Pr. In all presented experimental results, there is a significant contribution of CEF around temperature of 12 K, which can have a strong impact on the praseodymium state. In the studied alloys praseodymium behaves as lanthanum with two additional non-interacting $f$ electron. More interestingly, the parent compound PrCoGe$_3$ shows giant magnetoresistance, which is probably connected with the electronic band structure and reduced electrons mobility.

XPS measurements confirmed the successful synthesis of good quality samples of solid solutions for the Ce$_{1-x}$Pr$_x$CoGe$_3$ series. Co 2$p$ spectra demonstrate the absence of contribution of Co oxides and a close similarity with Co metal. The Pr/Co 3$d$ and 4$d$ XPS spectra point to a stable configuration of the Pr/Co 4$f$ shell in studied materials. The stable valence 3 for Pr and Ce is consistent with X-ray diffraction data and magnetic susceptibility measurements.

We presented the results of first-principles calculations for CeCoGe$_3$, Ce$_{0.5}$Pr$_{0.5}$CoGe$_3$ and PrCoGe$_3$. We considered non-spin-polarized models as the basis for XPS spectra and spin-polarized models to investigate magnetic properties. We shown that substitution of Pr for Ce significantly affects the electronic structure of the alloys.

(1) The calculations explain the evolution with Pr concentration of the measured Ce$_{1-x}$Pr$_x$CoGe$_3$ XPS spectra mainly as a change in the position and magnitude of 4$f$ contributions. (2) Mulliken electronic population analysis indicates electronic states of $f$-electron atoms as close to Ce $f^1$ and Pr $f^2$. (3) The charge analysis and calculated densities of states indicate that the chemical bonds in Ce$_{1-x}$Pr$_x$CoGe$_3$ alloys are mainly formed by Ce/Pr 5$d$, Co 3$d$, and Ge 4$p$ and 4$s$ orbitals. (4) The calculations indicate that charge transfer occurs mainly from 4$f$ elements towards Ge and Co sites.

The constructed magnetic phase diagram shows that the ordering temperature decreases monotonically with the increasing $x$ and the extrapolation to 0 K provides $x = 0.66$ for the phase transition $T_1$. The possibility of appearance of the NFL behaviour is very low, as the QCP scenario is excluded due to a reduction of energy of RKKY and Kondo interactions.

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