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Contribution of unstable valence states of europium to the electronic transport properties of $EuPd_{2-x}Si_{2+x}$

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The intermetallic alloy system $EuPd_{2-x}Si_{2+x}$ ($-0.2 \le x \le 0.75$) ($CeGa_2Al_2$ structure type) was studied by microstructure and compositional homogeneity analysis, X-ray absorption and diffraction at room temperature. Electrical resistivity and thermopower measurements were performed in the temperature range 5.0-300 K. According to data obtained by X-ray L_{III}-absorption spectroscopy, resistivity and thermopower measurements, we can state that with increasing Si content there is a transition from an intermediate valence state (IV), through a Kondo type state (KS), to a stable Eu^{2+} europium ion. We can also state that an intermediate valence state and a Kondo type state coexist at specific Pd/Si ratios. The decrease of the effective valence of the europium ion from 2.30 ($x = -0.2$) to almost 2.00 ($x = 0.75$) is accompanied by a decrease of the lattice parameter a and the a/c ratio. The investigation was carried out in the context of questions discussed for some time in the scientific community, namely: How is the transition type (stable europium ion – inter-configuration fluctuation state) related to the magnetic ordering state, Kondo type state, and to the intermediate valence state in this type of compound?

Intermetallics / Electron-electron interactions / Electronic transport / Kondo effect / Valence fluctuations

1. Introduction

The ternary compounds RM_2X_2 (where R is a rare-earth element, M is a transition element, X is another metal or a non-metal) and solid solutions based on these compounds have been widely investigated for deeper understanding of the strong electron-electron correlation phenomena in intermetallics. These compounds can have relatively wide homogeneity regions, which can influence the crystal growth process and, correspondingly, predefine the physical properties of the solid solutions [1]. For example, in the solid solution $Eu(Cu_{1-x}Ag_x)_2Si_2$ ($0 \le x \le 1$) one can suggest that the process of weakening of the magnetic order proceeds by gradual shrinking of the magnetic moment, rather than only in a way of degradation of the spatial correlation of the moments due to thermal agitation [2-4].

Taking into account some new aspects we decided to complete the investigation of partially studied series of systems, in particular $EuPd_{2-x}Si_{2+x}$.

The $EuPd_2Si_2$ compound is one of the most interesting and thus one of best investigated ones [5-10]. In this compound, europium is in an intermediate valence state having $\upsilon_{eff} = 2.23$. A large number of solid solutions formed by atomic substitution based on this compound have been synthesized and investigated. In an earlier work [1] we ascertained that the homogeneity region of this compound is located within the limits $-0.2 < x \le 0.75$. It seemed of interest to find a rule that describes the evolution of the electronic state of europium in the whole homogeneity region. Due to the reasons mentioned above, we decided to start a new investigation and extend it by new techniques.

2. Experimental details

Elements of the following purity were used for the synthesis: Eu 99.81 %, Pd 99.99 % and Si 99.999 %. The alloys were prepared by arc melting in an argon atmosphere under a pressure of 10^5 Pa with subsequent annealing at 700 K for 50 h. The crystal structure was studied using an X-ray diffractometer DRON-2 with Fe $K\alpha$ radiation. An aqueous solution of iron chloride was used as etching solution for the analysis of the microstructure using an optical microscope. Microscopic studies were conducted using a scanning electron microscope REMMA-102. Images were obtained in the composite mode (COMPO) using backscattered electrons. The elemental composition of the individual phases was obtained by X-ray energy-dispersive spectrometry (EDS). The valence state of the europium ions was investigated by X-ray L_{III}-absorption spectroscopy at $T = 300$ K. Electrical resistivity and differential thermopower were measured in the temperature range 5-300 K, using conventional methods. Magnetic properties were investigated using a vibrating sample magnetometer in the temperature range 80-400 K.

3. Experimental results and discussion: crystal structure, microstructure and composition

According to the X-ray diffraction analysis, all the alloys within the composition range $-0.2 < x \leq 0.75$ were single-phase with a crystal structure belonging to the $CeGa_2Al_2$ type. The only exception was the sample with the composition $EuPd_{2.2}Si_{1.8}$, which was two-phase. The substitution of silicon for palladium results in changes of the lattice parameters (Fig. 1). The lattice parameter a decreases and the parameter c increases with increasing silicon content. The unit cell volume remains almost constant.

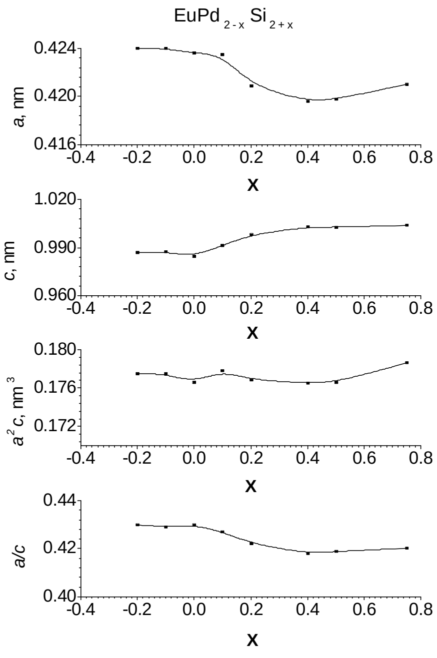


Fig. 1 Composition dependence of the lattice parameters of $EuPd_{2-x}Si_{2+x}$ alloys.

Besides the X-ray diffraction analysis, we analyzed the microstructure, composition and homogeneity of the alloys. Fig. 2 shows images of the microstructure obtained using an optical microscope and a scanning electron microscope (×150 magnification). Scanning electron microscope images with ×600 magnification are presented in Fig. 3.

For all the compositions, a block microstructure was observed. The large blocks usually contain extended, similarly oriented microblocks (microcrystallites) of approximate size 100 µm or more, as was observed for the $Eu(Cu_{1-x}Ag_x)_2Si_2$ compound. The composition of the microcrystallites is the same and homogeneous within a microcrystallite, again with the exception of the sample with the composition $EuPd_{2.2}Si_{1.8}$, which contains grains with excess Pd compared to the nominal composition. Inhomogeneities inside individual blocks of $EuPd_{2-x}Si_{2+x}$ were not observed for $x > 0$.

The intergrain boundaries are Pd-enriched for all of the alloys, except for stoichiometric $EuPd_2Si_2$, for which the intergrain boundaries are Eu-enriched and Si-depleted compared to the nominal composition. The best agreement between the composition inside the grains and at their boundaries was observed for the $EuPd_{1.25}Si_{2.75}$ sample. The overall composition estimated for the 200×200 µm^2 range agrees well with the nominal one, which allowed us to use the nominal compositions of the studied samples.

Physical properties

The lattice contraction within the rare-earth metal sublattice (parameter a, Fig. 1), due to composition variations caused by the replacement of Pd atoms by Si atoms, results in considerable transformations in the character of the temperature dependence of the kinetic properties of the alloys. The changes in the electronic structure of the crystal may be a result of changes in the valence of europium. Fig. 4 and Fig. 5 show X-ray L_{III}-absorption spectra for the $EuPd_{2-x}Si_{2+x}$ system ($x = -0.2$, 0.0, 0.75) and the determined effective valence of europium. The effective valence of europium decreases gradually from $\upsilon_{eff} = 2.30$ in $EuPd_{2.2}Si_{1.8}$ to $\upsilon_{eff} = 2.05$ in $EuPd_{1.8}Si_{2.2}$, and further towards $\upsilon_{eff} = 2.00$. Hence, the atomic substitution has allowed us to induce a process of transition of the europium ion from a stable state to a state of inter-configurational fluctuations. Pd-enriched crystals exhibit a tendency for an intermediate valence state of europium, and, in the other sense, an increase of the silicon concentration stabilizes the divalent state of europium.

The changes in the effective valence of europium depending on the composition are reflected in the kinetic properties of the alloys. The temperature dependencies of thermopower and resistivity of the $EuPd_{2-x}Si_{2+x}$ samples are presented in Figs. 6 and 7, respectively. The temperature dependence of the electrical resistivity indicates a metallic type of conductivity and it is clear that, besides the phonon contribution and residual resistivity, an additional

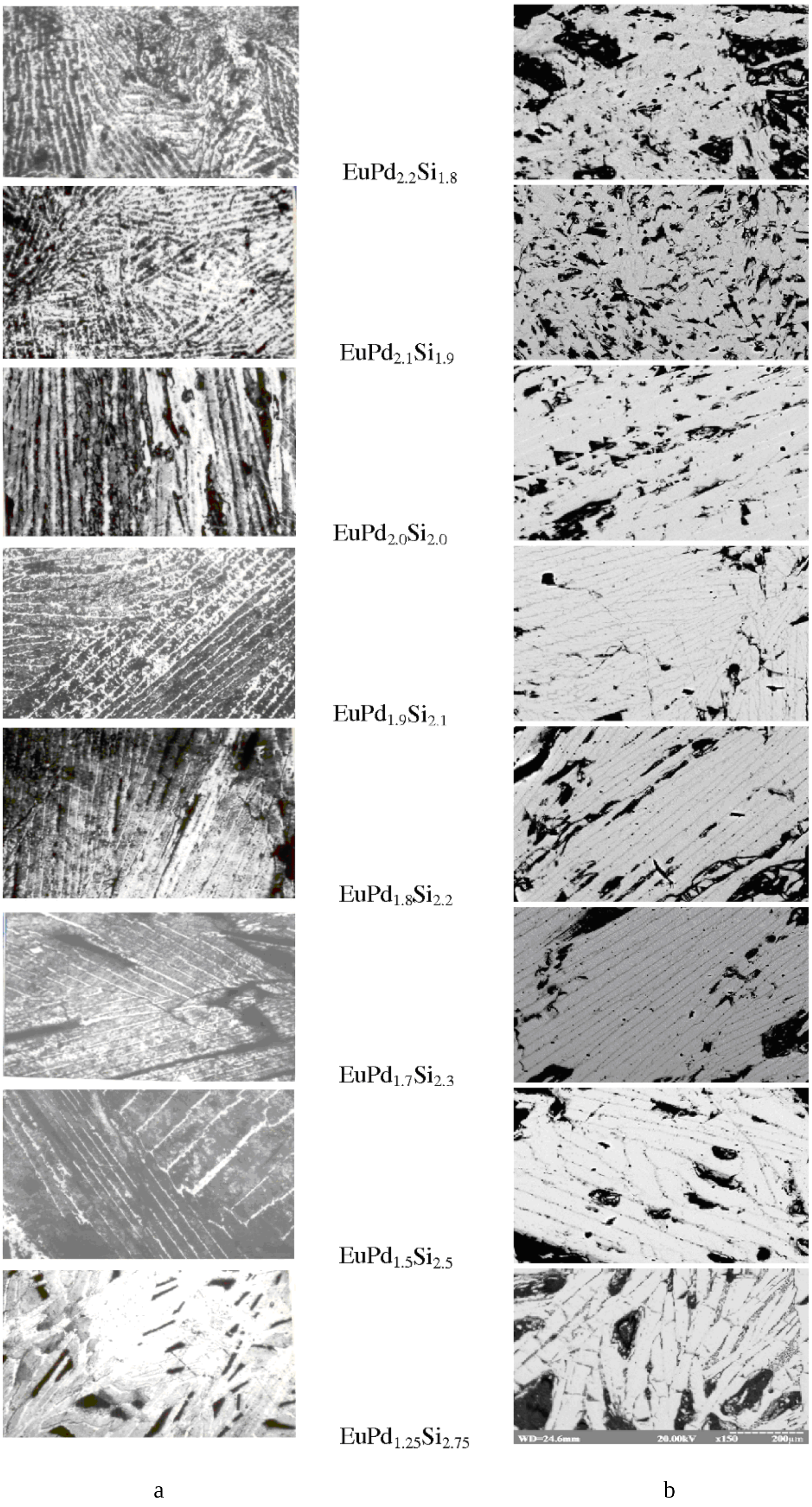
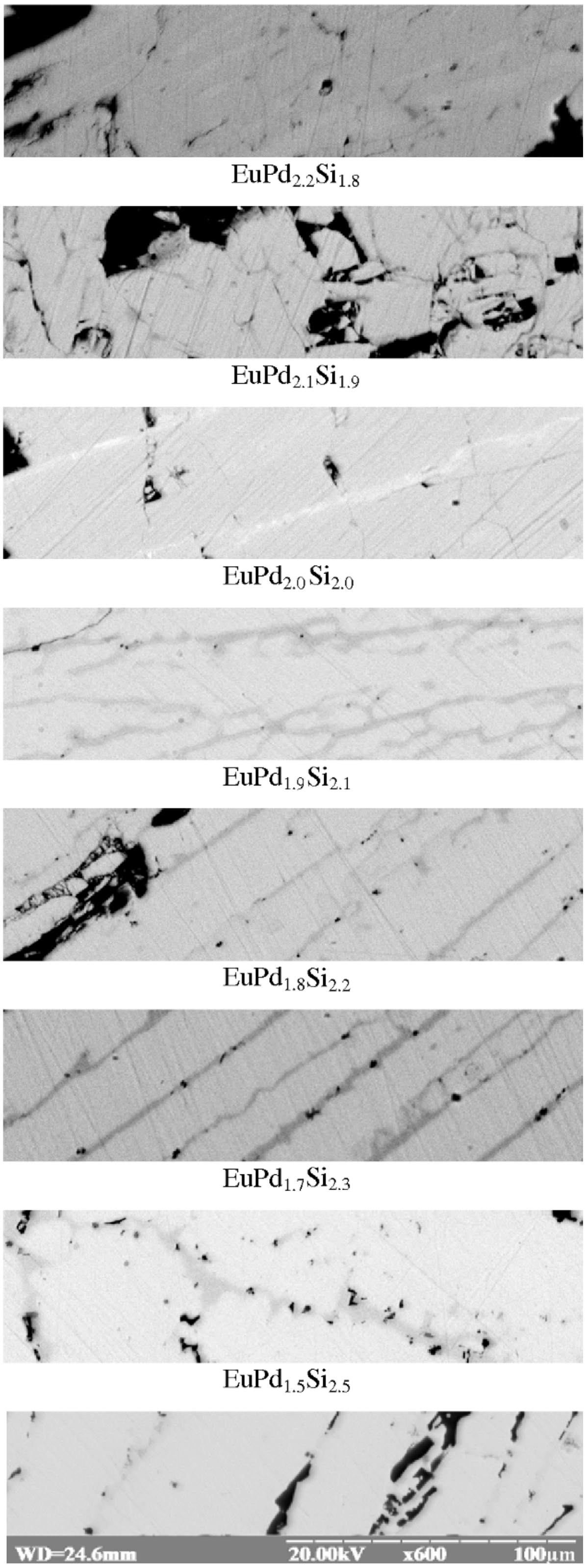


Fig. 2 $EuPd_{2-x}Si_{2+x}$ microstructure: (a) obtained by an optical microscope after chemical etching (scale ×150); (b) obtained by a scanning electron microscope (scale ×150).



$EuPd_{2.2}Si_{1.8}$

$EuPd_{2.1}Si_{1.9}$

$EuPd_{2.0}Si_{2.0}$

$EuPd_{1.9}Si_{2.1}$

$EuPd_{1.8}Si_{2.2}$

$EuPd_{1.7}Si_{2.3}$

$EuPd_{1.5}Si_{2.5}$

$EuPd_{1.25}Si_{2.75}$

Fig. 3 Quantitative and qualitative analysis of the composition performed using a scanning electron microscope (scale ×600).

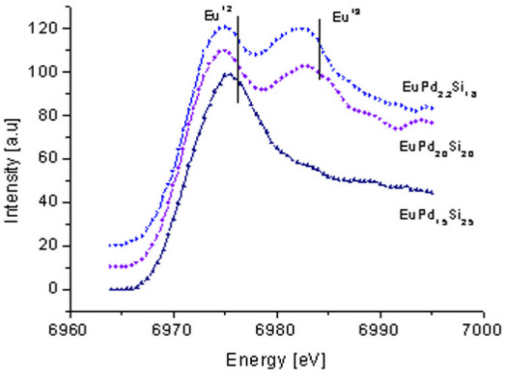


Fig. 4 X-ray L_{III}-absorption spectra of $EuPd_{2-x}Si_{2+x}$ alloys (x = -0.2, 0, 0.5).

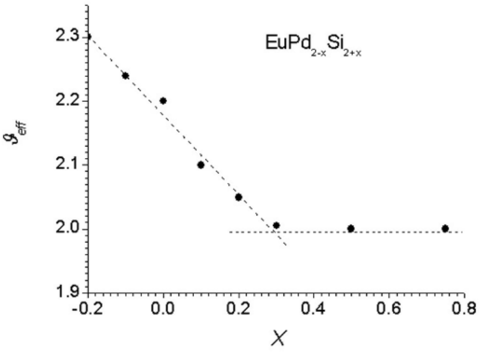


Fig. 5 Composition dependence of the effective valence of Eu (υ_{eff}) in $EuPd_{2-x}Si_{2+x}$ alloys at 300 K.

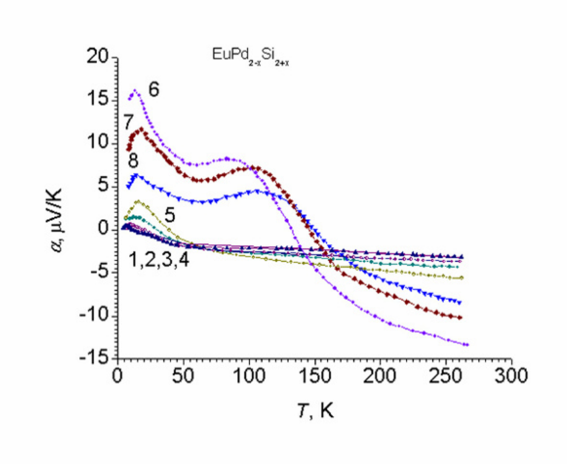


Fig. 6 Temperature dependence of the thermopower of $EuPd_{2-x}Si_{2+x}$ alloys:

1 – $EuPd_{1.25}Si_{2.75}$	5 – $EuPd_{1.9}Si_{2.1}$
2 – $EuPd_{1.5}Si_{2.5}$	6 – $EuPd_2Si_2$
3 – $EuPd_{1.7}Si_{2.3}$	7 – $EuPd_{2.1}Si_{1.9}$
4 – $EuPd_{1.8}Si_{2.2}$	8 – $EuPd_{2.2}Si_{1.8}$.

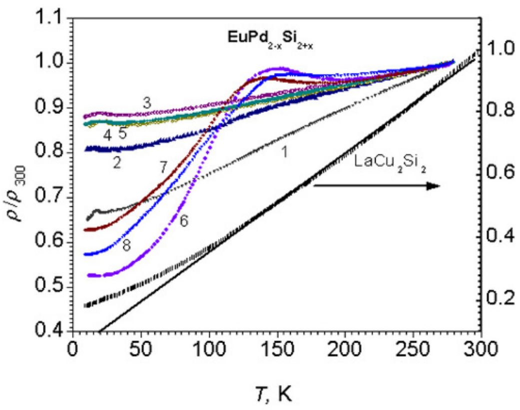


Fig. 7 Temperature dependence of the reduced resistivity ρ/ρ_{300} of $EuPd_{2-x}Si_{2+x}$ alloys:

1 – $EuPd_{1.25}Si_{2.75}$	5 – $EuPd_{1.9}Si_{2.1}$
2 – $EuPd_{1.5}Si_{2.5}$	6 – $EuPd_2Si_2$
3 – $EuPd_{1.7}Si_{2.3}$	7 – $EuPd_{2.1}Si_{1.9}$
4 – $EuPd_{1.8}Si_{2.2}$	8 – $EuPd_{2.2}Si_{1.8}$.

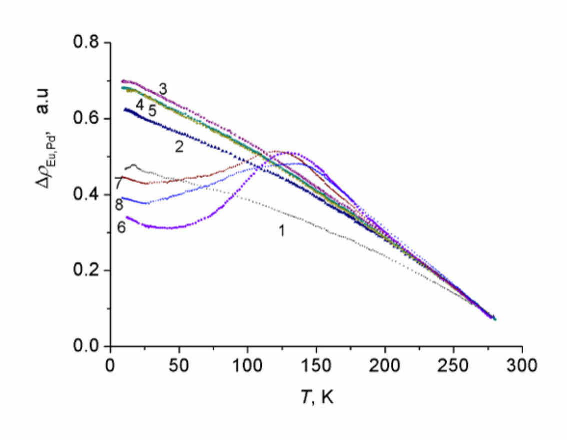


Fig. 8 Temperature dependence of $\rho_{mag}(T) \sim \Delta\rho_{Eu}(T) = \rho(T)/\rho_{300}\,(EuPd_{2-x}Si_{2+x}) - \rho(T)/\rho_{300}(LaCu_2Si_2)$:

1 – $EuPd_{1.25}Si_{2.75}$	5 – $EuPd_{1.9}Si_{2.1}$
2 – $EuPd_{1.5}Si_{2.5}$	6 – $EuPd_2Si_2$
3 – $EuPd_{1.7}Si_{2.3}$	7 – $EuPd_{2.1}Si_{1.9}$
4 – $EuPd_{1.8}Si_{2.2}$	8 – $EuPd_{2.2}Si_{1.8}$.

contribution, which we traditionally denote as $\rho_{mag}(T)$, is present:

$$\rho(T) = \rho_0 + \rho_{ph}(T) + \rho_{mag}(T)$$

The temperature dependence of the additional component of the resistivity, which corresponds to the influence of the *d*-shell of the transition metal and *f*-shell of the rare-earth metal (in particular the intermediate valence state of the europium ion), can be qualitatively described by subtracting the value of the resistivity of the isostructural analog $LaCu_2Si_2$ from the experimental resistivity of $EuPd_{2-x}Si_{2+x}$ (Fig. 8). We should emphasize that only the qualitative behavior of the temperature dependence of the additional contribution to the total resistance of the sample is regarded:

$$\rho_{mag}(T) \sim \Delta\rho_{Eu}(T) = \rho(T)/\rho_{300}(EuPd_{2-x}Si_{2+x}) - \rho(T)/\rho_{300}(LaCu_2Si_2) \quad (1)$$

Herewith we consider that an additional component $\rho_{mag}(T)$ is absent in the $LaCu_2Si_2$ case and the temperature dependence of the electrical resistivity can be described by the Bloch-Grüneisen law.

A qualitative difference between the samples with $x \leq 0$ and $x > 0$ is clearly seen from the temperature dependence of both the thermopower and the resistivity. The Pd-enriched samples, which, as shown above, contain europium in an intermediate valence state, show two maxima in the temperature dependence of the thermopower. The temperature dependence of the resistivity for this group of samples differs qualitatively from that of the other samples too. Since small variations of the lattice parameters (Fig. 1) have a dramatic impact on the temperature dependence of differential thermopower and resistance (presence or absence of a high-temperature peak) of the $EuPd_{1.9}Si_{2.1}$ and $EuPd_{2.1}Si_{1.9}$ samples (Figs. 6,7), one can suggest that in this case the coordination environment of the europium ion plays a much more significant role than just a "geometric" factor. The silicon atoms located at the palladium site, directly or indirectly, stabilize the divalent state Eu^{2+}.

The absence of a high-temperature maximum (on the thermopower temperature dependence of the $EuPd_{1.9}Si_{2.1}$ sample), which is attributed to the intermediate valence state of the europium ion, according to the L_{III}-spectroscopy data, precedes the transition of the europium ion to the divalent state. ^{151}Eu Mössbauer absorption spectra [10], obtained at 85 K for this composition, also indicate the divalent state of europium.

Some time ago, an increasing instability of the $4f^{\,7}$ configuration to the ground state was discovered based on Mössbauer spectroscopy data (isomeric shift and effective hyperfine field) in $Eu(Pd_{1-x}Au_x)_2Si_2$ for $0.18 \leq x \leq 1.0$. The Eu valence calculated according to L_{III}-absorption spectroscopy, does not agree well with the valence calculated from the Mössbauer isomeric shift or from the magnetic moment of the Eu ions. Abd-Elmeguid *et al.* [11] noted that a stable Eu^{2+} configuration is typical for the europium ion in $Eu(Pd_{1-x}Au_x)_2Si_2$ in the range $0.4 < x \leq 1$. In the range $0.18 \leq x < 0.41$, where the system is still antiferromagnetically ordered, the europium valence becomes intermediate. This instability can be caused by a partial expansion of the 4*f*-shell compared to the occupied 5*s* and 5*p* shells, which results in an enhancement of the 4*f*-(5*d*,6*s*)-hybridization, but not in a real shift of the 4*f*-layer. It was shown that an expansion of the 4*f*-level could directly change the lattice parameters and influence the Mössbauer isomeric shift.

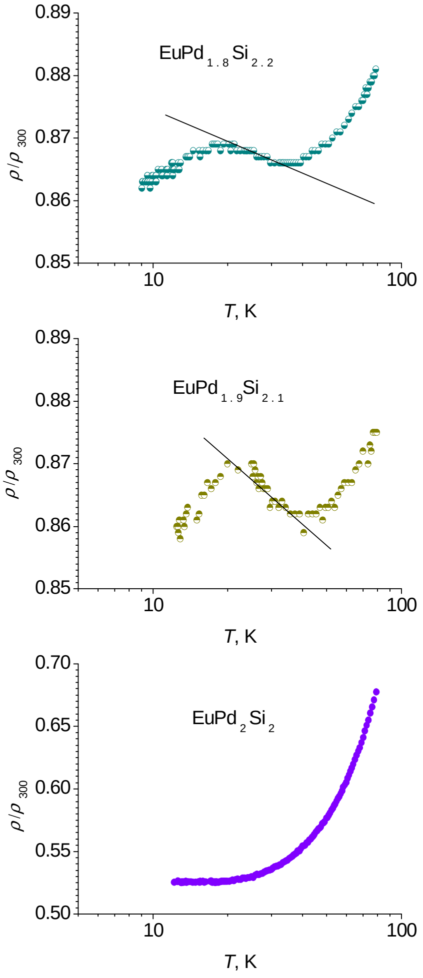


Fig. 9 Low-temperature range of the temperature dependence of reduced resistivity ρ/ρ_{300} of $EuPd_{2-x}Si_{2+x}$ alloys (x = 0.2, 0.1, 0).

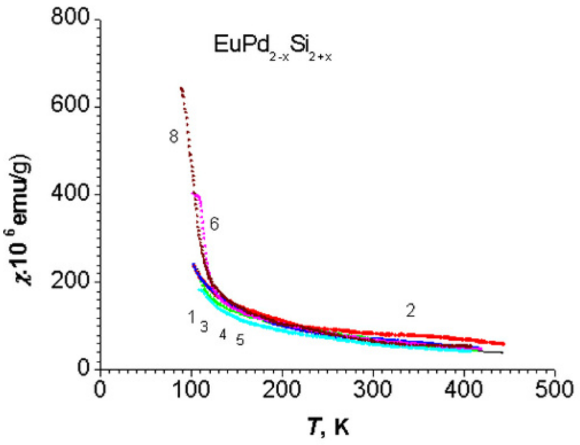


Fig. 10 Temperature dependence of the magnetic susceptibility of $EuPd_{2-x}Si_{2+x}$ alloys:

1 – $EuPd_{1.25}Si_{2.75}$	5 – $EuPd_{1.9}Si_{2.1}$
2 – $EuPd_{1.5}Si_{2.5}$	6 – $EuPd_2Si_2$
3 – $EuPd_{1.7}Si_{2.3}$	
4 – $EuPd_{1.8}Si_{2.2}$	8 – $EuPd_{2.2}Si_{1.8}$.

According to the europium L_{III}-spectroscopy data for $EuPd_{1.9}Si_{2.1}$, the effective valence υ_{eff} = 2.08(±0.02) approximately corresponds to a zero value of the excitation energy ε_{ex} ($Eu^{2+} \rightarrow Eu^{3+}$) within the ionic model, which means degeneration of the $4f^{7}$ and $4f^{6}$ configuration energies. We have already shown [1] that under these conditions the transition of europium from the magnetic Eu^{2+} regime to a regime of inter-configurational fluctuations can occur through a state of the concentrated Kondo system type. The presence of a low-temperature thermopower peak and a relatively large resistance with a Kondo feature (Fig. 9) at low temperatures serve as a proof for our assumption. One can suggest the coexistence of an intermediate valence state and a Kondo state in this system, as in other systems of this type [12].

The mismatch between the results of the different experiments (L_{III}-spectra and isomeric shift) can indicate possible belonging of some $EuPd_{2-x}Si_{2+x}$ alloy compositions to the “Kondo-lattice” class, which, however, change to a magnetically ordered state at low temperatures or have developed spin fluctuations. The disagreement was also analyzed in [8], where it was concluded that for many europium compounds of the EuM_2X_2 type the ground state can be magnetic for $\upsilon_{eff} < 2.33$ and an isomeric shift < -8.6. An $EuAg_{0,1}Cu_{1,9}Si_2$ sample with $\upsilon_{eff} \approx 2.34$ was not magnetically ordered even at 1.8 K [2].

The temperature dependence of the magnetic susceptibility of the samples of the $EuPd_{2-x}Si_{2+x}$ system is shown in Fig. 10. As a characteristic feature one should indicate an obvious deviation of this temperature dependence from the Curie-Weiss law of the $EuPd_2Si_2$ sample below 110 K, considering that the maximum speed of valence change is observed at temperatures close to 140 K [8]. Further characteristic features are the relatively large value of the susceptibility of the electronic gas and the large values of the effective magnetic moment (per formula unit) observed for palladium-enriched samples, *i.e.* for the samples containing europium in the intermediate valence state (see Table 1).

Conclusions

We can draw the following conclusions:

The $EuPd_{2-x}Si_{2+x}$ solid substitution solution exists in the homogeneity region $-0.2 < x \leq 0.75$, preserving the $CeGa_2Al_2$ structure type. Compared to $Eu(Cu_{1-x}Ag_x)_2Si_2$, inhomogeneities within the same microcrystal are less pronounced in $EuPd_{2-x}Si_{2+x}$. For a europium atom in any valence state, both the geometric factor (contraction or expansion of the crystal lattice) and the nearest neighborhood configuration are important. For $EuPd_{2-x}Si_{2+x}$, similarly to some other investigated compounds of the EuM_2X_2 type (and solid solutions based on them), silicon atoms that substitute for the *d*-element stabilize the divalent state of europium.

Table 1 Magnetic parameters [a] of $EuPd_{2-x}Si_{2+x}$ alloys.

No.	Composition	μ, μ_B		θ, K		C		$\chi(0)\cdot10^6$, emu/g
		CW	MCW	CW	MCW	CW	MCW	
1	$EuPd_{1.25}Si_{2.75}$	7.1		28		6.3		
2	$EuPd_{1.5}Si_{2.5}$	9.3	6.0	-40	43	11	4.4	36
3	$EuPd_{1.7}Si_{2.3}$	8.0		4		8		
4	$EuPd_{1.8}Si_{2.2}$	8.2	6.8	52	38	8.5	5.7	16
5	$EuPd_{1.9}Si_{2.1}$	7.6	6.8	5	27	7.3	5.7	9
6	$EuPd_2Si_2$ (150-450 K)	7.4	4.8	55	85	6.8	3.0	35
8	$EuPd_{2.2}Si_{1.8}$		5.8	62	75	6.6	4.2	23

[a] CW – Curie-Weiss law $\chi = C/(T-\theta)$; MCW – modified Curie-Weiss law $\chi = \chi(0)+C/(T-\theta)$; insignificant deviations from the CW law or MCW are ignored; μ – magnetic moment in Bohr magnetons per formula unit.

For $EuPd_{2-x}Si_{2+x}$, a transition of the europium ion from the stable state (Eu^{2+}) to an inter-configurational fluctuation state can be induced by component substitutions. This transition can occur *via* a state of the Kondo system type. Based on low-temperature resistivity data, the existence of a concentrated Kondo lattice type state in $EuPd_{2-x}Si_{2+x}$ has been established. In solid solutions that contain europium as a regular ion of the crystal matrix, a concentrated Kondo system type state can be observed when the effective valence reaches a critical value of $\upsilon_{eff} \approx 2.1$, which corresponds to the degeneration of the $4f^6$ and $4f^7$ configurations and to an excitation energy $\varepsilon_{ex}(Eu^{2+} \rightarrow Eu^{3+})$ approaching zero according to the ionic model. The amplitude of the interaction of itinerant electrons with the 4*f*-electrons depends on the type of the other components of the compound or solid solution.

While a transition of the system from an intermediate valence state to Eu^{2+} is induced by the change of composition, the high-temperature maximum in the thermopower disappears in many cases before the effective valence reaches an integer value (according to L_{III}-spectroscopy). We can suggest, based on own and literature data, that for EuM_2X_2-type compounds (and solid solutions based on them) with $CeGa_2Al_2$-type crystal structure there exists a boundary value of the effective valence ($\upsilon_{eff} = 2.30$) of the rare-earth element, below which the system can be in a Kondo type state and (or) magnetically ordered. The europium ion in $EuPd_{2-x}Si_{2+x}$, similarly as in other EuM_2X_2 compounds and solid solutions based on them, though occupying the same sites in the crystal lattice, can be characterized by energetically close, but still different electronic states.

Acknowledgements

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