

## Valence-Instable Ytterbium Compounds

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The description of chemical bonding in real space was recently extended from compounds with *s*- and *p*-elements to those with *d*-elements [1]. This allows a better bonding analysis in a large number of binary and ternary intermetallic phases containing transition metals. In case of rare-earth metals (*RE*) as a cationic component in such compounds, the electronic configuration of *RE* plays a crucial role for the formation of distinct structural patterns. During the investigation of stability of simple structural patterns derived from the  $AlB_2$  structure type, we observed, in particular on  $YbGa_2$ , that an electronic change of ytterbium can cause a structural transformation [2].

The question of valence instability of ytterbium in the sense of heavy fermion behavior was discussed in detail in the literature [3], however, the bonding aspects of this problem are still analyzed insufficiently. As a first part of a research project in this field we present here the results of detailed experimental investigations of the electronic configuration of ytterbium (depending on pressure and temperature) in some ternary compounds with relatively simple structures containing a transition metal (*TM*) and gallium. The ytterbium content increases from  $YbNiGa_4$  to  $YbAuGa$ , the Yb: *TM* ratio is constant 1:1.

X-ray absorption spectroscopy (XAS) was performed at the HASYLAB at DESY. The diamond-anvil cells used for generation of high hydrostatic pressures were modified according to specific requirements (see “X-ray Absorption Spectroscopy (XAS)”).

### $YbNiGa_4$

Compounds with the composition  $RENiGa_4$  ( $RE = Sm - Lu, Y$ ) have previously been found by investigations of the phase relations in the respective ternary systems [3]. On the basis of powder X-ray diffraction (XRD) data it could be shown that the crystal structures of these phases belong to the  $YNiAl_4$  type [4]. The ytterbium compound  $YbNiGa_4$  forms peritectically at 1133 K. For sam-

ples annealed at 873 K there is no indication for the presence of any homogeneity range, since no alterations ( $> 3$  e.s.d.) of the lattice parameters of the phase could be detected in two-phase and three-phase regions. The crystal structure was established from single crystal and powder XRD data: space group  $Cmcm$ ,  $a = 4.0866(1)$  Å,  $b = 15.2823(2)$  Å,  $c = 6.5046(1)$  Å,  $R_F = 0.025$  for 383 symmetrically independent reflections,  $R_{Bragg} = 0.066$  for 135 symmetrically independent reflections. The structure (Fig. 1) shows very short distances between nickel and gallium atoms:  $d(Ni-Ga) = 2.34$  Å. Other short interatomic distances are:  $d(Yb-Ga) = 2.93$  Å,  $d(Yb-Ni) = 3.14$  Å,  $d(Yb-Yb) = 4.09$  Å,  $d(Ga-Ga) = 2.60$  Å and  $d(Ni-Ni) = 3.93$  Å. The nickel and gallium atoms form a 3D network, in whose larger cavities ( $CN = 17$ ) ytterbium atoms are located.

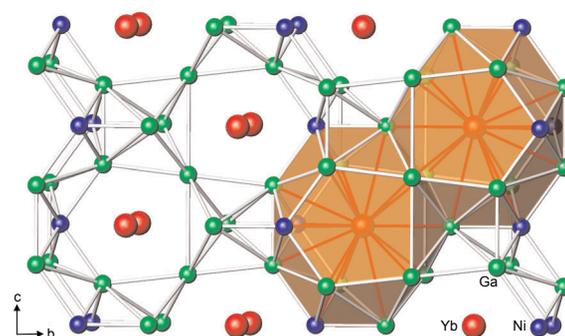


Fig. 1: Ytterbium atoms in the cages ( $CN = 17$ ) of the Ga,Ni-framework in the  $YbNiGa_4$  structure.

At ambient temperature, this phase shows a small paramagnetic susceptibility  $\chi$ , which starts to increase slightly with temperature above  $T \nearrow 240$  K. At low temperatures,  $\chi(T)$  increases strongly without attaining a magnetically ordered state for  $T > 1.8$  K and fields as small as 2 mT. A qualitative evaluation of the susceptibility data hints at an intermediate valency of the ytterbium atoms (Fig. 2). Magnetic measurements indicate that ytterbium is in a ground state close to  $4f^4$  and nickel is non-magnetic. For this reason, the com-

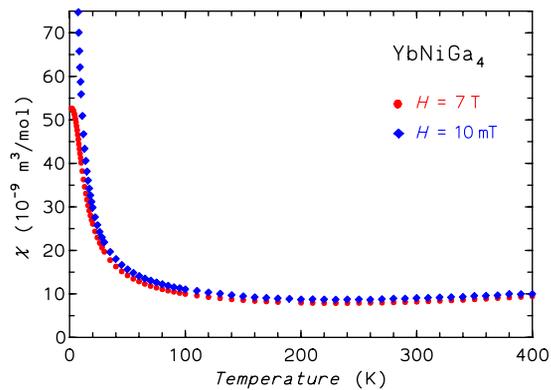


Fig. 2: Magnetic susceptibility vs. temperature for  $\text{YbNiGa}_4$ .

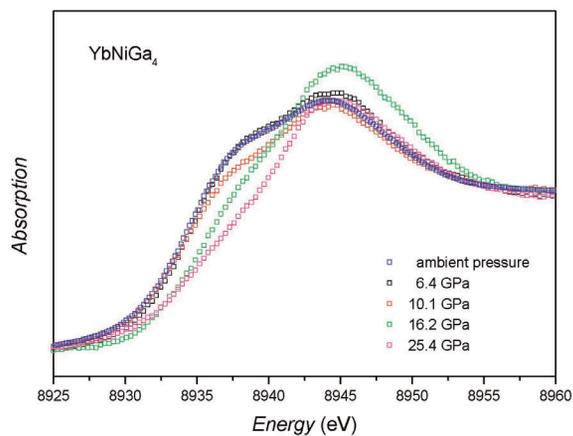


Fig. 3: Yb  $L_{\text{III}}$  XAS spectra for  $\text{YbNiGa}_4$  at different pressures.

compound  $\text{YbNiGa}_4$  was selected for further investigations of the pressure dependence of the valence state with XAS measurements. The X-ray absorption spectra (Fig. 3) at ambient pressure, 6.4 GPa, 10.1 GPa and 16.4 GPa display a characteristic two-peak structure, which reveals the presence of Yb in the  $4f^{14}$  ( $\text{Yb}^{2+}$ ) and  $4f^{13}$  ( $\text{Yb}^{3+}$ ) states. The peak at lower energy levels ( $\text{Yb}^{2+}$ ) becomes smaller with rising pressure, so that at 25.4 GPa only the higher energy maximum is detectable. The absence of the low-energy maximum in the spectrum at 25.4 GPa proves the absence of the  $4f^{14}$  ( $\text{Yb}^{2+}$ ) state. Hence, the pressure-dependent conversion of  $\text{Yb}^{2+}$  into  $\text{Yb}^{3+}$  in  $\text{YbNiGa}_4$  is completed at this pressure.

## $\text{YbNiGa}_2$

Two series of samples with compositions in the range of  $\text{Yb}_{25}\text{Ni}_{22-30}\text{Ga}_{53-45}$  ( $\text{YbNi}_{1\pm x}\text{Ga}_{2\mp x}$ ) were produced to investigate the structural stability of  $\text{YbNiGa}_2$  (MgCuAl<sub>2</sub> type of structure, Fig. 4). The first series was annealed at 1073 K for two weeks, the second one at 873 K for four weeks. The evaluation of the powder XRD data showed a homogeneity range  $\text{Yb}_{25}\text{Ni}_{25\pm 2}\text{Ga}_{50\pm 2}$  whose extent is independent of the homogenization temperature. The refinement of the lattice parameters confirms this observation since an increase in the volume of the unit cell ( $V_{\text{cell}}$ ) with increasing gallium content is observed (Fig. 5). A remarkable feature is the

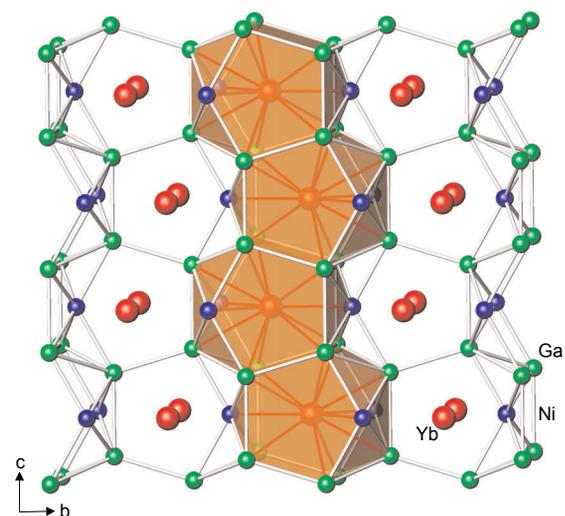


Fig. 4: Ytterbium atoms in the cages ( $\text{CN} = 13$ ) of the Ga, Ni-framework in the  $\text{YbNiGa}_2$  structure.

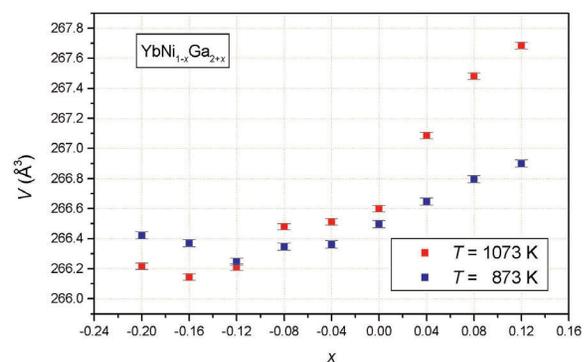


Fig. 5: Unit cell volume  $V$  vs. gallium content in the  $\text{YbNi}_{1-x}\text{Ga}_{2+x}$  phase (annealing temperatures 1073 K and 873 K).

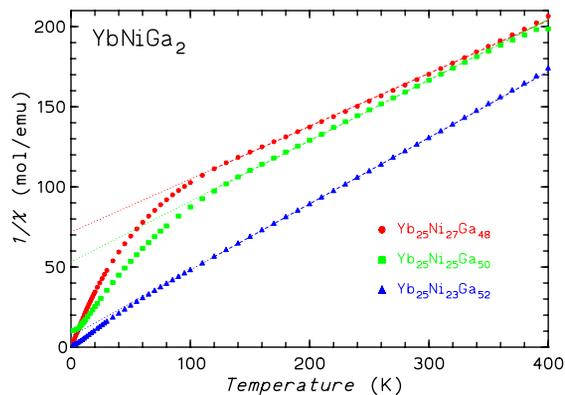


Fig. 6: Inverse magnetic susceptibility vs. temperature for  $\text{YbNi}_{1\pm x}\text{Ga}_{2\mp x}$  (annealing temperature 1073 K).

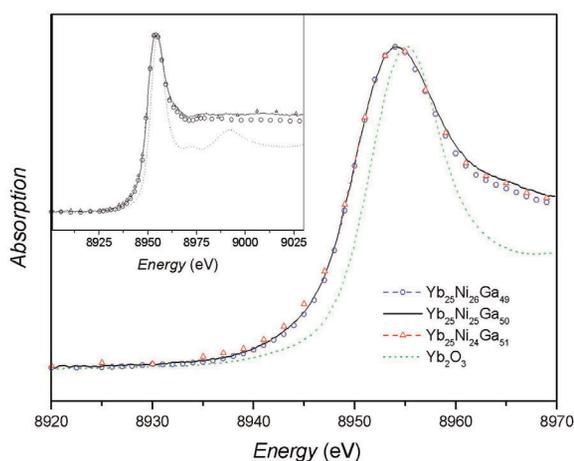


Fig. 7:  $\text{Yb } L_{\text{III}}$  XAS spectra for  $\text{YbNi}_{1\pm x}\text{Ga}_{2\mp x}$  at ambient temperature.

strong increase of  $V$  for gallium contents higher than 50 at.% in the samples annealed at 1073 K in contrast to those annealed at 873 K. This behavior can be explained by the fact that on the gallium-rich side the variation in  $V$  is caused exclusively by the substitution of nickel by gallium ( $r_{\text{Ni}} < r_{\text{Ga}}$ ). On the nickel-rich side the variation of  $V$  is smaller, since the substitution is antagonistically accompanied by a valence change of the ytterbium ( $r_{\text{Yb}^{2+}} > r_{\text{Yb}^{3+}}$ ). This interpretation of the crystallographic data is confirmed by temperature-dependent measurements of the magnetic susceptibility on the samples annealed at 1073 K.

The behavior of the sample rich in gallium  $\text{Yb}_{25}\text{Ni}_{23}\text{Ga}_{52}$  is similar to a Curie-Weiss law ( $\mu_{\text{eff}}/\text{Yb} = 4.4 \mu_{\text{B}}$ ,  $\theta_{\text{p}} = -17$  K). The magnetism is more com-

plicated for the composition  $\text{Yb}_{25}\text{Ni}_{25}\text{Ga}_{50}$  ( $\mu_{\text{eff}}/\text{Yb} = 4.5 \mu_{\text{B}}$ ,  $\theta_{\text{p}} = -131$  K). In the case of the sample rich in nickel ( $\text{Yb}_{25}\text{Ni}_{27}\text{Ga}_{48}$ ) the presence of  $\text{Yb}^{2+}$  is clearly observable at low temperature (Fig. 6).

The X-ray absorption spectra of the samples annealed at 873 K are almost identical (Fig. 7). They are dominated by a maximum shifted by 1 eV compared to the spectrum of the ternary reference sample  $\text{Yb}_2\text{O}_3$ . The absence of a second peak in the spectra shows, in accordance with the magnetic susceptibility, that the samples do not contain a larger amount of ytterbium  $4f^{14}$  ( $\text{Yb}^{2+}$ ) at ambient temperature. The shift of the main maximum is, however, caused by the different character of the chemical bonding of Yb in the oxidic reference  $\text{Yb}_2\text{O}_3$  compared to the intermetallic compounds studied.

## YbAgGa<sub>2</sub>

As another representative of intermetallic phases with the composition of  $\text{RETMGa}_2$ , the compound  $\text{YbAgGa}_2$  was examined with regard to a pressure-induced change on the valence electron configuration of ytterbium.  $\text{YbAgGa}_2$  should show a polymorph character with valence change of Yb in different modifications [6]. The following data are observed for the high-temperature  $\beta$ -modification. While the crystal structure of  $\text{YbNiGa}_2$  is of the  $\text{MgCuAl}_2$  type, a variant of the  $\text{ScRhSi}_2$  structure type was found for  $\beta$ - $\text{YbAgGa}_2$  (Fig. 8). The crystal structure is orthorhombic, space group  $Pnma$ ,  $a = 6.9653(3)$  Å,  $b = 4.3362(2)$  Å,  $c = 10.3386(4)$  Å.

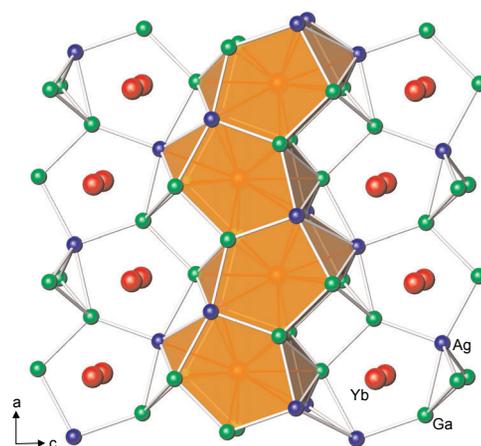


Fig. 8: Ytterbium atoms in the cages (CN=14) of a Ga,Ag-network in the  $\text{YbAgGa}_2$  crystal structure.

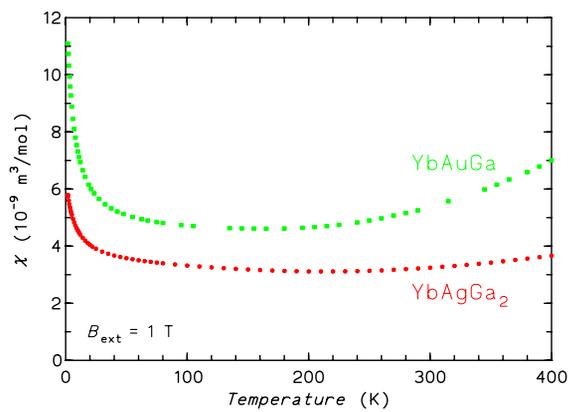


Fig. 9: Magnetic susceptibility of  $\text{YbAgGa}_2$  and  $\text{YbAuGa}$  vs temperature.

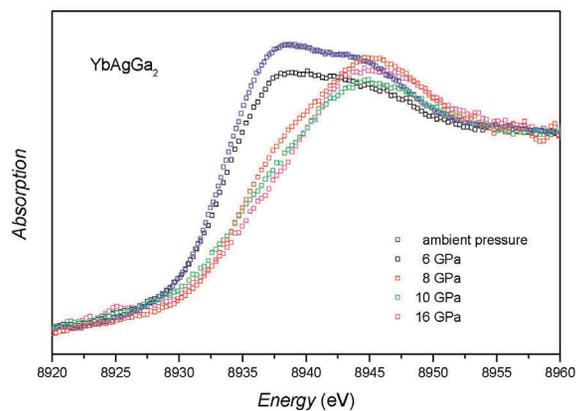


Fig. 10:  $\text{Yb } L_{\text{III}}$  XAS spectra for  $\text{YbAgGa}_2$  structure at different pressures.

The structure displays the following shortest distances between atoms:  $d(\text{Yb-Ga}) = 3.014 \text{ \AA}$ ,  $d(\text{Yb-Ag}) = 3.183 \text{ \AA}$ ,  $d(\text{Yb-Yb}) = 3.832 \text{ \AA}$ ,  $d(\text{Ga-Ga}) = 2.622 \text{ \AA}$ ,  $d(\text{Ga-Ag}) = 2.720 \text{ \AA}$  and  $d(\text{Ag-Ag}) = 3.024 \text{ \AA}$ .

The qualitative evaluation of the susceptibility measurement (Fig. 9) reveal an intermediate valence of the ytterbium atoms at room temperature which can be confirmed by the X-ray absorption behavior at the  $\text{Yb } L_{\text{III}}$  edge (Fig. 10). In the XAS spectrum at ambient pressure and at 6 GPa, two distinct peaks can be detected, proving the presence of both  $\text{Yb}^{2+}$  ( $4f^{14}$ ) and  $\text{Yb}^{3+}$  ( $4f^{13}$ ) states. With increasing pressure, the peak at lower energy becomes significantly smaller, so that at 16 GPa only the high-energy peak is detectable indicating the complete conversion of  $\text{Yb}^{2+}$  into  $\text{Yb}^{3+}$ .

## YbAuGa

In comparison with the above mentioned compounds  $\text{YbNiGa}_4$ ,  $\text{YbNiGa}_2$  and  $\text{YbAgGa}_2$ , the phase  $\text{YbAu}_x\text{Ga}_{2-x}$  with  $x \neq 1$  has the largest content of ytterbium.  $\text{YbAuGa}$  was reported previously to adopt the  $\text{KHg}_2$  structure type. [7].

For an investigation of the structural stability, the samples with compositions in the range of  $\text{YbAu}_x\text{Ga}_{2-x}$  ( $x = 0.21$  up to 1.29) were synthesized. The analysis of the powder XRD patterns shows a rather complex phase relation in the system. In

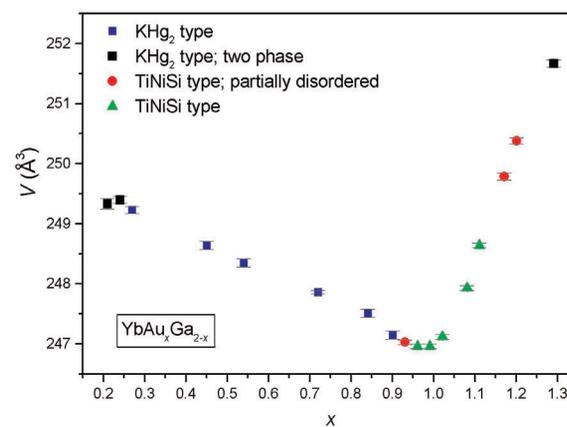


Fig. 11. Unit cell volume  $V$  and structure type vs  $x$  in  $\text{YbAu}_x\text{Ga}_{2-x}$ .

contrast to the previous investigation, the structure of  $\text{TiNiSi}$  was found for compositions around  $x = 1$  and the  $\text{KHg}_2$  structure was observed for lower gold content ( $0.25 < x < 0.9$ ) (Fig. 11).

At smaller Au contents, the lattice parameter refinements from powder XRD data show a contraction of the unit cell volume with increasing Au:Ga ratio. This behavior is observed up to the equiatomic composition. In contrast, a pronounced unit cell expansion is found in the high Au content region of the homogeneity range (Fig. 11). This unusual minimum in the unit cell volume is accompanied by structural disorder with increasing deviation from the 1:1:1 composition. The crystal structure of  $\text{YbAuGa}$  as determined from single crystal XRD data ( $R_{\text{F}} = 0.029$ , 426 symmetrically independent reflections) belongs to the  $\text{TiNiSi}$  type: space group  $Pnma$ ,  $a = 7.1167(3) \text{ \AA}$ ,  $b = 4.5019(3) \text{ \AA}$ ,  $c = 7.7083(3) \text{ \AA}$  with complete and ordered occupation of all atomic sites (Fig. 12). Beside different atomic radii ( $r_{\text{Au}} > r_{\text{Ga}}$ ), which cause the increase of

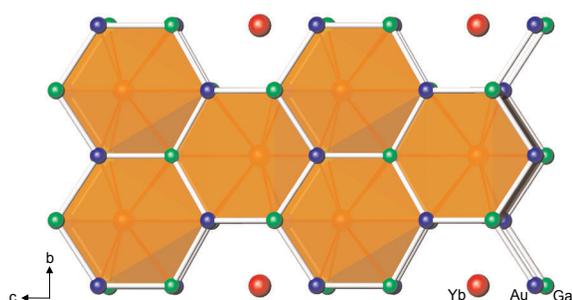


Fig. 12: Ytterbium atoms in the cages (CN = 12) of the Ga,Au-network in the YbAuGa structure.

the unit cell volume with increasing substitution of Ga by Au, more complicated atomic interactions have to be taken into account to explain the structural disordering as well as the unit cell volume behavior at smaller Au contents.

The magnetic susceptibility between 1.8 K and 400 K was measured at zero pressure and the X-ray absorption at the Yb  $L_{III}$  edge was established at isostatic pressures of up to 24.4 GPa. The XAS

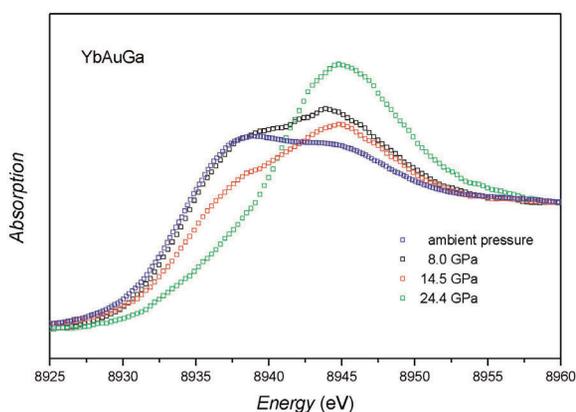


Fig. 13: Yb  $L_{III}$  XAS spectra for YbAuGa at different pressures.

spectra at ambient pressure, 8 GPa and 14.5 GPa clearly reveal a two-peak structure (Fig. 13), which, in accordance with the magnetization measurements (Fig. 9), is characteristic for the presence of both the  $4f^{14}$  and  $4f^{13}$  configurations ( $Yb^{2+}$  and  $Yb^{3+}$ ) in YbAuGa. The maximum in the spectrum at lower energies, which reflects the state  $4f^{14}$  ( $Yb^{2+}$ ), decreases in intensity with increasing pressure. The vanishing of the second maximum in the spectrum at 24.4 GPa shows that no detectable portion of  $Yb^{2+}$  ions is present in YbAuGa and is thus a proof of a pressure-induced valence change of  $Yb^{2+}$  into  $Yb^{3+}$ .

In all four investigated compounds, the ytterbium atoms were found to be near to the stability limit of the  $4f^{14}$  configuration. This limit can easily be crossed. Even small changes of the composition lead to a change of the electronic configuration of Yb at low temperatures in  $YbNi_{1\pm x}Ga_{2\mp x}$ . Moderate pressures are sufficient to complete the transformation  $4f^{14} \rightarrow 4f^{13}$  in  $YbNiGa_4$ ,  $YbNiGa_2$ ,  $YbAgGa_2$  and YbAuGa.

## References

- [1] M. Kohout, F. Wagner, Yu. Grin, *Theor. Chem. Acc.* **108**, 150 (2002).
- [2] U. Schwarz *et al.*, *Z. Anorg. Allg. Chem.* **627**, 2249 (2001).
- [3] Z. Fisk, B. Maple, *J. Alloys Compd.* **183**, 303 (1992).
- [4] Ya. P. Yarmolyk, Yu. Grin, *Izv. AN SSSR. Metally*, No **5**, 228 (1981).
- [5] Yu. Grin, K. Hiebl, P. Rogl, C. Godart, *J. Alloys Compd.* **239**, 127 (1996).
- [6] Yu. Grin, M. Ellner, K. Hiebl, B. Baumgartner, P. Rogl, *J. Alloys Compd.* **221**, 125 (1995).
- [7] S. K. Malik, D. T. Adroja, B. D. Padalia, R. Vijayarayanan. In: *Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions*. Edg. L. C. Gupta, S. K. Malik. Plenum Press, 1996, p. 463.