# Possible Intelligent Materials Based on Compounds with Valence-Unstable Rare-Earth Elements

I. D. Shcherba, H. Noga*, and L. V. Bekenov**

*Ivan Franko National University of Lviv,*
*8 Kyryla & Mefodiya Str.,*
*UA-79005 Lviv, Ukraine*
*\*Institute of Technology, University of Pedagogy,*
* 2 Podchorazych Str.,*
* PL-30084 Krakow, Poland*
*\*\*G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine,*
* 36 Academician Vernadsky Blvd.,*
* UA-03142 Kyiv, Ukraine*

Intelligent materials occupy a special place among the huge number of known materials and those, which are being created all the time. Despite the impressive number of publications, no attempt has yet been made to classify compounds with a valence-unstable rare-earth element (R.E.) as smart materials. In this review paper, we show that the valence of the R.E. in some compounds can be changed by external and internal factors, such as temperature, pressure, changes in the occupation of $d$- and $f$-levels, and changes in the coordination polyhedra of atoms. Changing the valence of the R.E. may significantly alter the electrical and magnetic properties of compounds.

**Key words:** mixed valence, smart materials, x-ray absorption, ytterbium, cerium.

Інтелектуальні матеріяли займають особливе місце серед величезної кількости відомих матеріялів і тих, що постійно створюються. Незважаючи на значну кількість публікацій, досі не було зроблено жодної спроби класифікувати сполуки з валентно нестабільним рідкісноземельним елементом (Р.Е.) як розумні матеріяли. У цій оглядовій статті ми показуємо, що валентність Р.Е. у деяких сполуках може змінюватися зовнішніми та внут-

Corresponding author: Ivan Dmytrovych Shcherba
E-mail: ishcherba@gmail.com

рішніми чинниками, такими як температура, тиск, зміни в заповненні $d$- й $f$-рівнів, зміни в координаційних поліедрах. Змінення валентности Р.Е. може істотно міняти електричні й магнетні властивості сполук.

**Ключові слова:** змішана валентність, розумні матеріяли, рентґенівське поглинання, Ітербій, Церій.

## 1. INTRODUCTION

The purpose of this paper, based on the review of a considerable number of research papers on the physics of compounds with intermediate valence, is to demonstrate that such compounds may be attributed to such a wide class of materials that are commonly referred to as intelligent materials [1, 2].

First, consider one of the most important conceptual features according to which it has been customary to classify certain substances as intelligent materials. It is the presence of interdependent but inherently different properties (mechanical, electrical, magnetic, *etc.*) that makes diverse materials 'smart'. This allows these materials to be used either as sensors, sensitive to a given external impact, or as actuators, transmitting the impact from the control device to the controlled object. In both cases, the impact response function is usually non-linear. Some of the smart materials can respond independently to external impact. One example is the bimetallic plates in the simplest temperature controllers. In this case, the 'intelligence' of the material manifests itself in having a 'memory', *i.e.*, the ability to restore the original shape, which the object had before plastic deformation, during which this shape was changed. In some cases, the intelligent materials open up new fields of science and technology and determine the fundamental performance of the most complex devices. In particular, the very small movements of the probe in a scanning tunnelling microscope cannot be achieved by mechanical systems. This is where smart materials with a piezoelectric effect come in.

The most difficult part of creating intelligent materials and systems based on them is providing feedback between the external impact and the object's response. Materials become 'intelligent' when the sensing and actuating elements built on their basis are combined into an intelligent structure to achieve the required advanced functionality.

Over the past decades, a separate field of research has emerged in solid state physics on a new class of intermetallic compounds with strong interelectron correlations, known as heavy fermions, Kondo lattices, and systems with valence instability. The study of the phenomena of this class of materials containing some rare earth (Ce, Eu, Yb) or actinide (U, Np) elements is mainly concerned with the interac-

tion of partially filled localized $f$-states with each other and with the band states of the crystal matrix. At low temperatures, the coupling between localized and band states can be multi-particle in nature, leading to the formation of a narrow resonance in the density of states near the Fermi level. This corresponds to the emergence of a separate group of charge carriers with large effective masses, which are manifested by anomalous behaviour of the main magnetic, thermophysical, and transport properties.

It is particularly important to note that very different ground states (superconductor, dielectric, band magnetics, heavy Fermi liquid, *etc.*) can be realized in compounds of this class, depending on the properties of the crystal matrix. This allows treating these systems as unique objects for the study of several functional questions about the nature of cooperative phenomena in solid state physics.

At present, the ground state of the above intermetallic systems is not well understood, and no theory has been developed to describe them quantitatively at the microscopic level. When describing physical properties, theoretical models often make conflicting assumptions about the role of individual interactions in a crystal.

The available experiments are mainly devoted to the study of a rather narrow range of known Kondo systems and do not allow us to trace in detail the effect of a number of characteristic parameters of the crystal matrix on the formation of the ground state. Particularly, insufficient attention has been given to the study of Kondo lattices containing magnetically active $d$-elements of the iron group. The presence of transition $3d$-elements in such systems enables controlled changes in several important parameters of the energy spectrum of the crystal matrix and the ground state characteristics of the Kondo $f$-centres by means of certain atomic substitutions. Also relevant in this area is the search for new Kondo systems with well-defined magnetic f-sublattices of different dimensions.

Apart from the purely theoretical interest in the intermediate valence state as such, there are many areas where such compounds have wide practical applications, for example, in information storage systems, as well as heat energy converters or efficient catalysts.

## 2. DISCUSSION

Using a series of examples, we are going to show the dependence of the valence of a R.E., as the main parameter of valence instability, on several external factors. The revealed instability of the valence state of the R.E. on temperature, pressure, occupation of $d$ ($f$) levels, changes in the coordination environment, and other factors cause changes in the physical and chemical properties of the R.E. compound. In our view, this means that intermetallic compounds with an unstable valence of the

R.E. ions may be included in a subgroup of smart materials.

## 2.1. The External Pressure-Induced Change in the Valence Value

It is well known that Ce can exist in several phases [3]. We are interested in $\gamma$-, $\alpha$- and $\alpha'$-phases, of which the first two have the f.c.c. structure; at room temperature, a $1^{st}$ kind transition occurs between them at a pressure of 7.5 Kbar with significant hysteresis. In the $\gamma$-phase, cerium is practically trivalent. The phase transition is accompanied by a jump-like change in volume of $\cong 15\%$; at the same time, magnetic properties, resistance, thermal and electrical EMF, *etc.* change dramatically. The $\alpha$-phase, however, does not correspond to the total valence of Ce; from the lattice parameter values and other data, it was found that immediately near the transition, the Ce valence in the $\alpha$-phase is $\cong 3.67$. The occupation of the *f*-level continues to decrease with increasing pressure, up to a value of 3.85, and then, at $P = 40$ Kbar, a phase transition to a new phase $\alpha'$, which already has a valence of $\cong 4+$, occurs.

Let us now move on to the analysis of compounds containing valence-unstable ytterbium. Figure 1 shows the variation of ytterbium
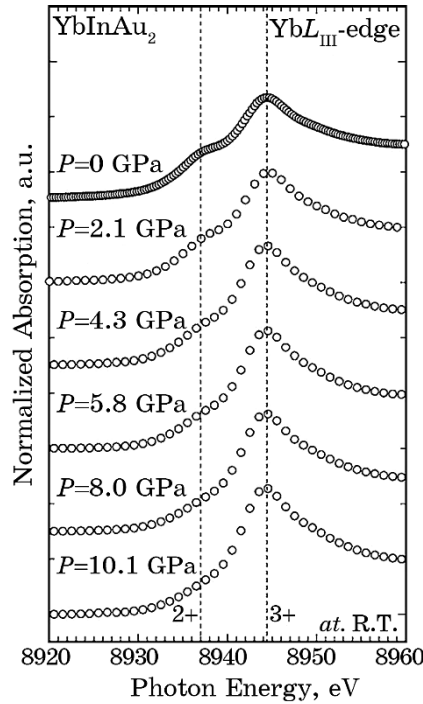


**Fig. 1.** Yb $L_{III}$ XANES spectra of YbInAu$_2$ at various pressures and room temperature.

valence in the YbInAu$_2$ compound with pressure [4]. For this compound, the valence of ytterbium changes with increasing pressure from the state of intermediate valence ($P = 0$ GPa) to the integer valence, namely 3+.

## 2.2. The Temperature-Induced Change in the Valence Value

The effect of changing the Eu valence on the demagnetization process in the EuAg$_2$Si$_2$ compound was investigated in [5] (Fig. 2). Strong $4f$ and conduction-electron correlations enforce valence instability of europium in EuCu$_2$Si$_2$ and EuPd$_2$Si$_2$. Doping with silver and platinum, respectively, drives these systems at the verge of first order valence transition where the competition between magnetic ordering and valence instability becomes very clear [6]. With the increasing silver concentration in EuCu$_{2-x}$Ag$_x$Si$_2$, the time averaged europium $4f$-elelectronic configuration is driven closer toward the divalent state.

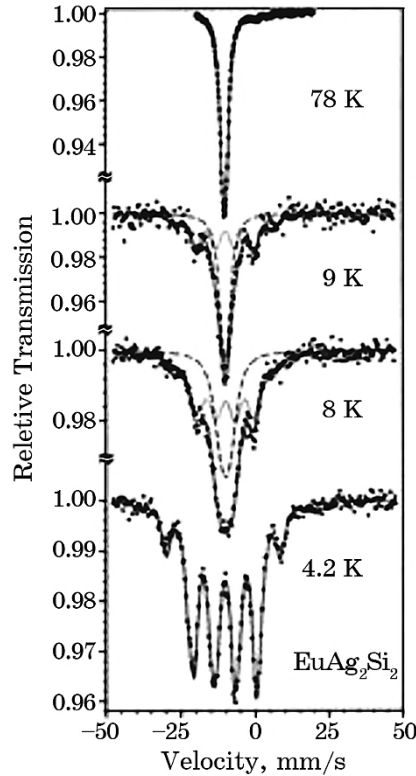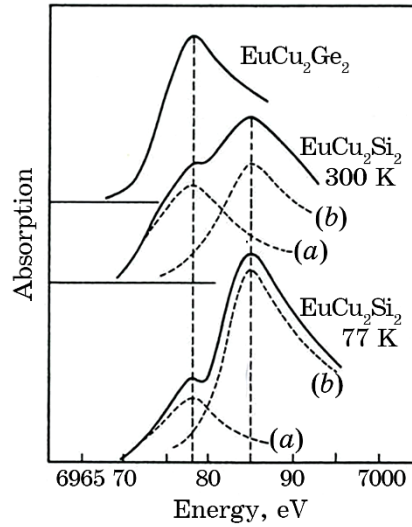The paper [7] shows that the valence of Eu changes not only with an



**Fig. 2.** $^{151}$Eu Mössbauer spectra for EuAg$_2$Si$_2$ at several temperatures.

**Fig. 3.** X-ray absorption spectra for the intermediate valence compound EuCu$_2$Si$_2$ at 300 K and 77 K. The spectra allow for distinguishing both configurations due to the exceedingly short observation time of the method [7].

external factor (temperature) but also with changes in the $p$-element (Fig. 3). The latter is very surprising since both silicon and germanium do not differ in the occupancy of outer orbitals.

The paper [8] reports on the synthesis of single crystals of EuCu$_2$Si$_2$ from an indium flux. In contrast to the previous studies [7] of polycrystalline samples, in which the intermediate-valence behaviour of Eu is reported, it is found that in single crystals of EuCu$_2$Si$_{20}$the behaviour of Eu is divalent, including the presence of antiferromagnetic order at 10 K.

## 2.3. The Dependence of the R.E. Valence on the Structural Type of a Compound

The electrical resistance, thermal EMF and magnetic susceptibility of the compounds YbNi$_4$In and YbNiIn$_4$ with valence-unstable Yb were measured at temperatures of 4.2–300 K in Ref. [9] (Fig. 4). The valence state of Yb was identified by measuring the x-ray $L_{\mathrm{III}}$ absorption spectra at $T = 300$ K (Fig. 5). It was shown that YbNi$_4$In has a Kondo magnetic lattice and exhibits crystal-field effects. The preferred scheme is the splitting of the $4f$ level of Yb$^{3+}$ with the doublet formation in the ground and first excited states. In the case of YbNiIn$_4$, a valence-unstable state of Yb is formed that does not make significant additional contributions to the transport coefficients.
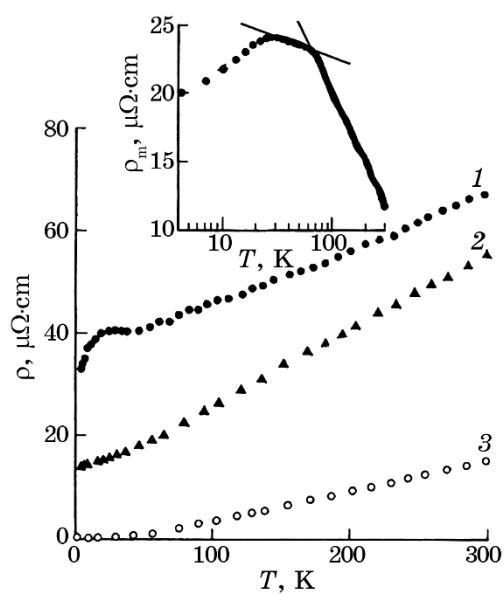
**Fig. 4.** Temperature dependences of the electrical resistance of $R\text{Ni}_4\text{In}$ [$R = \text{Yb}$ (*1*), Nd (*2*)] and $\text{YbNiIn}_4$ (*3*). The inset shows the magnetic contribution to the overall electrical resistance of valence unstable Yb on a logarithmic temperature scale.
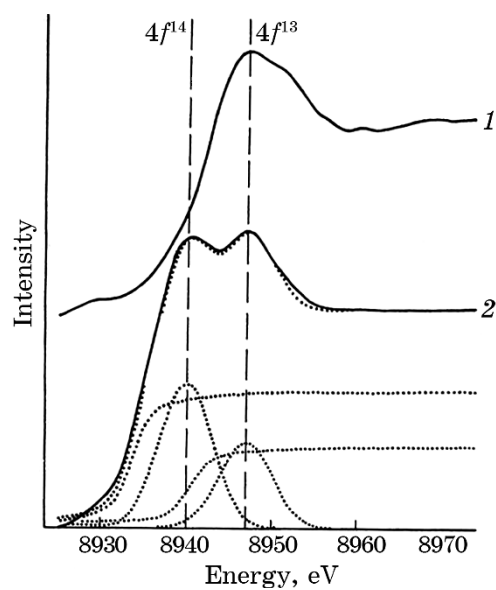
**Fig. 5.** The x-ray $L_{\text{III}}$ edge of Yb in $\text{YbNi}_4\text{In}$ (*1*) and $\text{YbNiIn}_4$ (*2*) and their resolutions into components (dotted curves).
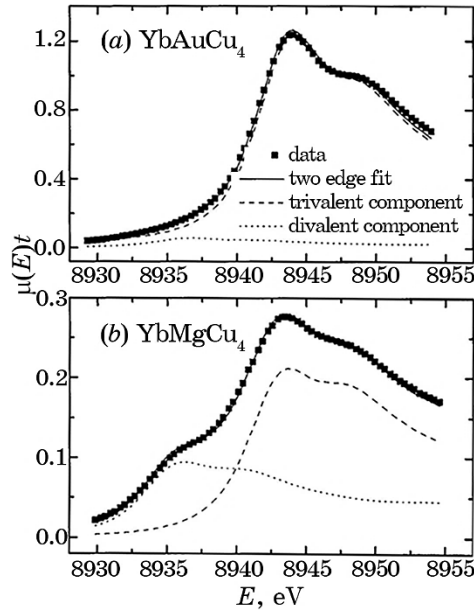
**Fig. 6.** The example of absorption data and their fits to the divalent and trivalent components of the Yb $L_{III}$-edge [10].

## 2.4. The Dependence of the R.E. Valence on the Second Component of Ternary Intermetallic Compounds

a) $YbTCu_4$ ($T$ = Au and Mg)

Reference [10] and Figure 6 present the results of the dependence of ytterbium valence on the second component of ternary intermetallic compounds, which nevertheless retain their type of crystal structure.

b) $Yb_2T_3Sn_5$ ($T$ = Pt and Pd)

In Reference [11], the valence states and thermoelectric properties of $Yb_2T_3Sn_5$ ($T$ = Pt and Pd) with two inequivalent Yb sites were studied. For $Yb_2Pt_3Sn_5$, the $4f$-hole occupancy number $n_f$ is estimated to be 0.4 at 300 K based on the magnetic susceptibility and $L_{III}$-edge absorption spectrum (Fig. 7).

## 2.5. The Effect of $d$- and $f$-Level Occupancy on the Valence State of Ce and Yb in Compounds with the $ThMn_{12}$ Structure

The $L_{III}$ x-ray absorption spectra (77 and 300 K) and magnetic susceptibility measurements were performed for $RM_4Al_8$ compounds in [12]. The mixed valence state of Ce was observed in $CeM_4Al_8$ with $M$ = Cr, Mn, and Fe. In the case of $M$ = Cu the $Ce^{3+}$ state is stabilized, but the Yb-based compound shows an intermediate valence ($\nu_{Yb}$ = 2.5). In the
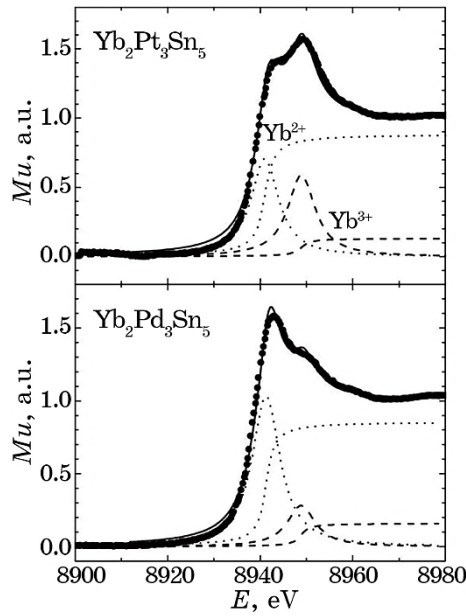
**Fig. 7.** The x-ray $L_{III}$-edge of Yb at 300 K for $Yb_2T_3Sn_5$ ($T$ = Pt and Pd) [11].

other Yb-based compounds, the Yb ion is mainly in the trivalent state (Fig. 8). The temperature dependence of the magnetic susceptibility of $RFe_4Al_8$ compounds fits the Curie–Weiss law over a wide temperature range (Fig. 9).

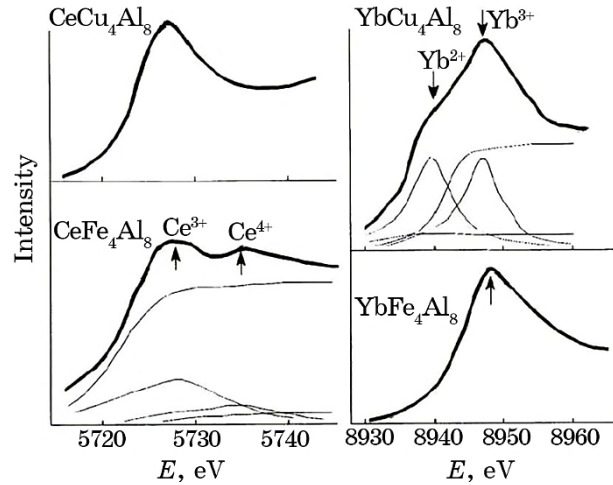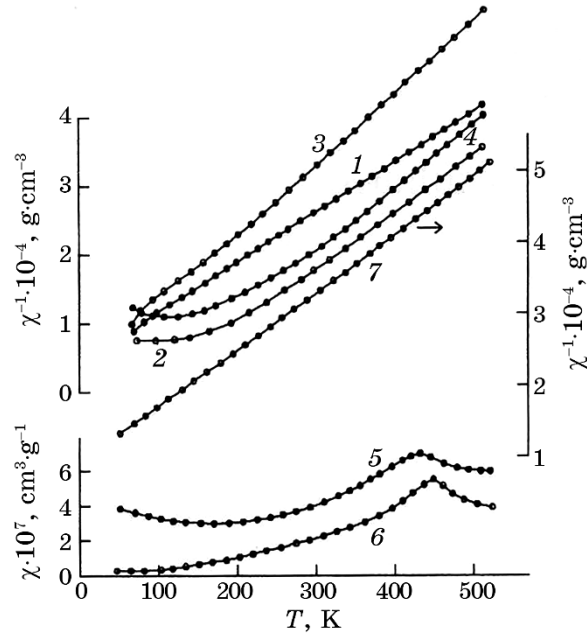Similar results were obtained in [13], where the temperature-



**Fig. 8.** The x-ray absorption $L_{III}$ spectra of Ce and Yb in $RM_4Al_8$ compounds.

**Fig. 9.** Magnetic susceptibility curves for $RM_4Al_8$: La (*1*), Ce (*2*), Yb (*3*), Y (*4*) and $RCu_4Al_8$: Yb (*5*), Y (*6*), Ce (*7*).

dependent specific heat, magnetic susceptibility, and resistance measurements were carried out to study the electronic state of Yb ion in $Yb_2Ni_{12}(P, As)_7$. All the measurements identify a valence fluctuating state for Yb in both compounds [13].

The x-ray photoelectron spectroscopy (XPS) and magnetic susceptibility ($\chi$) of $CeNi_2Al_3$ and of the reference compound $YNi_2Al_3$ were reported in [14]. Both the valence band and core level spectra were analysed.

### 2.6. The Dependence of the R. E. Valence on the Occupation of *d*-Levels

The x-ray absorption spectrum at the Yb $L_{III}$-edge and x-ray emission spectra of Ni and P at the $K$ and $L_{III}$-edges were studied experimentally and theoretically in the mixed valent compound $YbNi_2P_2$ with the $ThCr_2Si_2$-type crystal structure [15, 19]. The electronic structure of $YbNi_2P_2$ was investigated using the fully relativistic Dirac linear muffin-tin orbital (LMTO) band-structure method. It was shown that the individual $Yb^{2+}$ or $Yb^{3+}$ related x-ray absorption spectra contain the weights of 0.73 and 0.27, respectively (Fig. 10).

Compounds of the same structural type ($ThCr_2Si_2$), namely $RNi_2Ge_2$
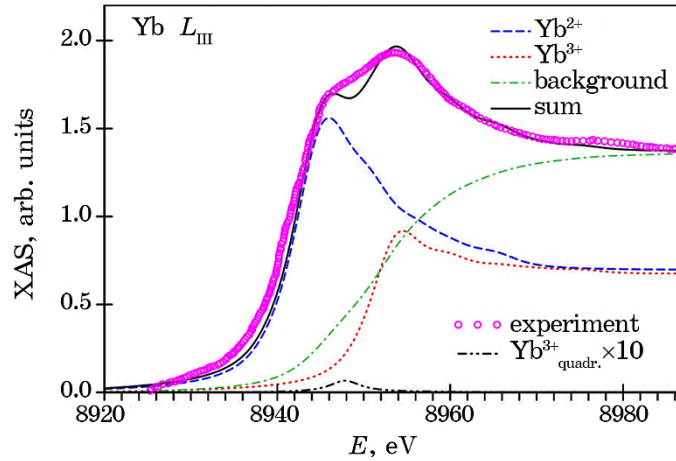
**Fig. 10.** The x-ray Yb $L_{III}$ absorption spectrum (open circles) in YbNi$_2$P$_2$ measured at 300 K compared with the theoretically calculated ones for trivalent (the full blue line) and divalent (the dashed red curve) Yb ions. The dashed-dotted black curve presents the spectrum from the electric quadrupole $2p \rightarrow 4f$ transitions for the Yb$^{3+}$ solution multiplied by 10.

($R$ = Dy, Ho and Er) and YbNi$_2$Si$_2$, were studied in Ref. [16].

Although strongly correlated $f$-electron systems are well known as reservoirs for quantum phenomena, a persistent challenge is to design specific states. What is often missing are simple ways to determine whether a given compound can be expected to exhibit certain behaviours and what tuning vector(s) would be useful to select the ground state. The authors of Ref. [17] address this question by aggregating information about Ce, Eu, Yb, and U compounds with the ThCr$_2$Si$_2$ structure. They construct electronic/magnetic state maps that are parameterized in terms of unit cell volumes and $d$-shell filling, which reveal useful trends including that (i) the magnetic and nonmagnetic examples are well separated, and (ii) the crossover regions harbour the examples with exotic states. These insights are used to propose structural/chemical regions of interest in these and related materials, with the goal of accelerating discovery of the next generation of $f$-electron quantum materials.

The results of a comprehensive study of the magnetic properties of the single crystal compound YbCo$_2$Si$_2$ are presented in Ref. [18]. The data obtained confirm the stable trivalent state of Yb and the nonmagnetic state of Co in the compound. A significant anisotropy of the magnetic susceptibility $\chi(T)$ was observed, whose moment in the ground plane is twice that in the $c$ direction. The combination of this result with the previously published neutron scattering data places strong constraints on the values of the crystal electric field parame-

**TABLE 1.** The valence of Ce and Yb in some compounds.

| Compounds | Structure | Valence, $T = 78$ K | Valence, $T = 300$ K |
|---|---|---|---|
| $CeCr_4Al_8$ | $ThMn_{12}$ | 3.18 | 3.15 |
| $CeMnAl_8$ | $ThMn_{12}$ | 3.13 | 3.19 |
| $CeFe_4Al_8$ | $ThMn_{12}$ | 3.20 | 3.26 |
| $CeCu_4Al_8$ | $ThMn_{12}$ | 3.05 | 3.08 |
| $YbFe_4Al_8$ | $ThMn_{12}$ | 3.00 | 3.00 |
| $YbCu_4Al_8$ | $ThMn_{12}$ | 2.46 | 2.48 |
| $YbNi_4In$ | $MgSnCu_4$ | 3.00 | 3.00 |
| $YbNiIn_4$ | $YNiIn_4$ | 2.30 | 2.37 |
| $YbNiGa_4$ | $YNiIn_4$ | 2.67 | 2.62 |
| $YbCu_{0.5}Ga_{3.5}$ | $BaAl_4$ | 2.18 | 2.11 |
| $YbPd_{0.5}Ga_{3.5}$ | $BaAl_4$ | 2.17 | 2.20 |
| $YbAg_{0.375}Ga_{3.62}$ | $BaAl_4$ | 2.27 | 2.26 |
| $YbAu_{0.5}Ga_{3.5}$ | $BaAl_4$ | 2.14 | 2.14 |

ters. The magnetic ordering in the $YbCo_2Si_2$ compound at $T_N \cong 1.65$ K was found to have the antiferromagnetic nature.

## 3. CONCLUSIONS

The presented results of the study of the valence state of the R.E. in some compounds (see also Table 1) give rise to certain conclusions about their possible classification as a subgroup of smart materials. It should be noted that the manifestation of unusual properties of Ce, Eu, and Yb in many compounds is associated with the presence of anomalies in their electronic configurations arising from the partial delocalization of $4f$-electrons and can initiate the transition to the states with intermediate valence.

We demonstrate that the valence of the R.E. in some compounds can be changed by external and internal factors, namely, (*a*) temperature (*e.g.*, cerium, $EuCu_2Si_2$, $EuAg_2Si_2$), (*b*) pressure ($YbInAu_2$), (*c*) the change of the occupation of $d$- and $f$-levels (compounds with the $ThCr_2Si_2$ or $ThMn_{12}$ structure), (*d*) the change of coordination polyhedra of atoms ($YbNi_4In$, $YbNiIn_4$).

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