

---

Proceedings of the National Conference on Neutron Scattering and the Complementary  
Methods in the Investigations of the Condensed Phases, Chlewiska 2007

## Mixed-Valence State in $\text{Yb}_2\text{CuGe}_6$

A. SZYTUŁA<sup>a</sup>, M. KONYK<sup>b</sup>, B. PENC<sup>a</sup> AND A. WINIARSKI<sup>c</sup>

<sup>a</sup>M. Smoluchowski Institute of Physics, Jagiellonian University  
Reymonta 4, 30-059 Kraków, Poland

<sup>b</sup>Department of Inorganic Chemistry, Ivan Franko National University of Lviv  
Kyryla and Mefodiya 6, UA-79005 Lviv, Ukraine

<sup>c</sup>A. Chełkowski Institute of Physics, University of Silesia  
Uniwersytecka 4, 40-007 Katowice, Poland

*Dedicated to Professor Jerzy Janik on the occasion of his 80th birthday*

We present here temperature dependent X-ray photoemission measurements on polycrystalline  $\text{Yb}_2\text{CuGe}_6$ . The analysis of these data shows the change in the effective valence, determined directly from the  $4f$  intensity ratio, as a function of temperature.

PACS numbers: 71.20.Lp, 75.20.Hr, 79.60.-i

### 1. Introduction

Rare-earth intermetallic compounds containing ytterbium exhibit a wide range of interesting and unusual physical and magnetic properties. This occurs mainly as a result of their mixed-valence state (II/III) or of changes from one valence state to the other.

The  $\text{Yb}_2\text{CuGe}_6$  compound investigated in this work belongs to the  $\text{R}_2\text{TGe}_6$  family, where T is Mn, Ni and Cu. These compounds crystallize in an orthorhombic crystal structure of the  $\text{Ce}_2\text{CuGe}_6$ -type (space group  $Amm2$ ) [1, 2].

In this work we present the results of X-ray photoemission spectroscopy (XPS) measured as a function of temperature. From this data the change of electronic structure is determined.

### 2. Experimental details

Measurements were carried out on polycrystalline sample prepared as reported previously [1]. XPS spectra were obtained at room temperature using a Multipurpose Electron Spectrometer PHI 5700/660 with Al  $K_\alpha$  monochromatized radiation ( $h\nu = 1486.6$  eV). The total energy resolution of the spectrometer with a hemispherical energy analyzer was about 0.3 eV for Ag  $3d$ . The spectrome-

ter was calibrated using Au  $4f_{7/2}$  (84.0 eV), Ag  $3d_{5/2}$  (368.27 eV) and Cu  $2p_{3/2}$  (932.66 eV) core-level photoemission spectra. Measurements were carried out in the temperature range 223–523 K. The vacuum during the measurements was about  $10^{-9}$  Torr.

The Shirley method [3] was used to subtract the background and such prepared experimental spectra were numerically refined using a model of 80% Gaussian and 20% Lorentzian.

### 3. Results

Figure 1 shows the XPS spectrum of  $\text{Yb}_2\text{CuGe}_6$  measured at room temperature in the binding energy range 0–1400 eV. The binding energy is related to the Fermi level ( $E_F = 0$ ). Except of the peaks corresponding to the appropriate levels of the individual constituting elements a small contamination by oxygen and carbon is visible.

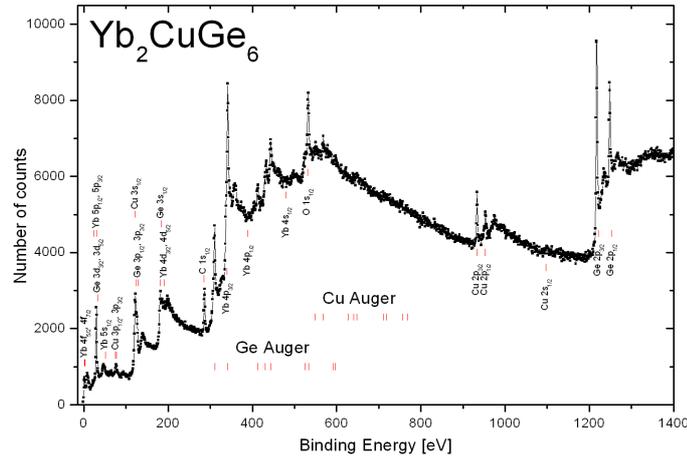


Fig. 1. XPS Al  $K_\alpha$  spectrum of  $\text{Yb}_2\text{CuGe}_6$  compound at room temperature in the wide binding energy range of 0–1400 eV.

The XPS valence bands (VBs) of  $\text{Yb}_2\text{CuGe}_6$  measured at different temperatures are shown in Fig. 2. The intermediate valence state of the Yb atoms can be corroborated by the valence spectrum. We observe two sets of peaks: between  $E_F$  and 4 eV, and between 6 and 12 eV. The first set of peaks corresponds to the spin-orbit doublet of the divalent Yb with the peaks at 0.25 and 1.50 eV for  $4f_{7/2}$  and  $4f_{5/2}$ , respectively. The spin-orbit splitting is about 1.25 eV, which is comparable to the other in ytterbium compounds. The peak at 4.3 eV is certainly due to the Cu  $3d$  states. Concerning the structure between 6 and 12 eV below  $E_F$ , we are convinced that the multiplet is due to the  $4f^{13} \rightarrow 4f^{12}$  transition.

Apparently, the intensity of the  $\text{Yb}^{3+}$  part is comparable with that of the  $\text{Yb}^{2+}$  part, suggesting that the Yb atoms in the studied compound are in-between

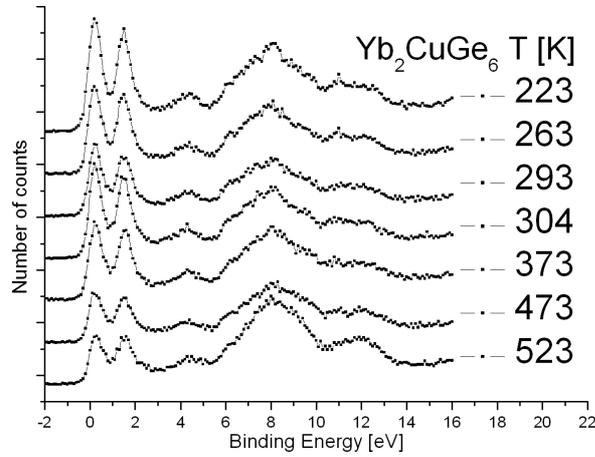


Fig. 2. XPS spectra of valence bands of  $\text{Yb}_2\text{CuGe}_6$  in the temperature range 223–523 K.

divalent and trivalent states. With increasing temperature the intensity of the peaks corresponding to  $\text{Yb}^{2+}$  state decreases while the peaks corresponding to  $\text{Yb}^{3+}$  increase. The intensity of Cu 3d peaks does not change with changing temperature. The positions of the peaks do not change with increasing temperature.

Figure 3 shows the Yb 4d spectra with a complex structure. The peaks at 181.2 and 190 eV correspond to the Yb  $4d_{5/2}$  and Yb  $4d_{3/2}$  states for  $\text{Yb}^{2+}$  while the peaks at 186 eV and those in the region of 195–210 eV correspond to  $\text{Yb}^{3+}$ . The intensity of the peaks corresponding to the  $\text{Yb}^{3+}$  state increases with increasing temperature.

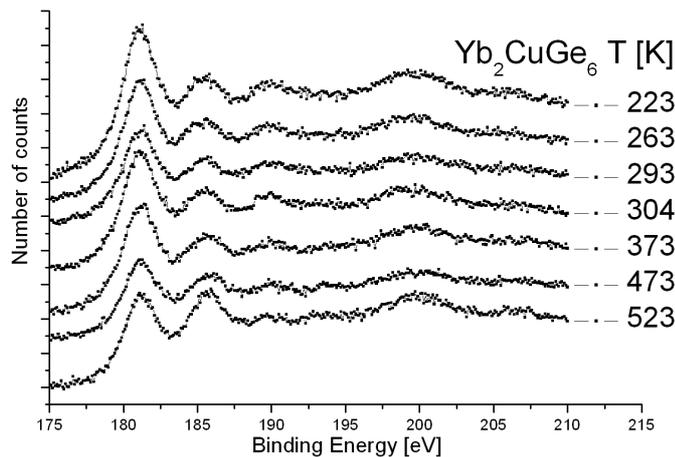


Fig. 3. Yb 4d core level photoemission spectra of  $\text{Yb}_2\text{CuGe}_6$  as a function of temperature in the range 223–523 K.

The presented XPS spectra indicate a mixed-valence state which is changed with increasing temperature. The valence  $v$  of Yb ions was estimated from the intensity ratio of the trivalent and the divalent part of the spectra via the relation [4]:

$$v = 2 + \frac{I(+3)}{\frac{13}{14}I(+2) + I(+3)},$$

where  $I(+2)$  and  $I(+3)$  are the integrated intensities of the divalent and trivalent peaks, respectively. Applying this formula to the XPS data yields values of the effective valence  $v$  as a function of temperature (see Fig. 4). Below the room temperature (RT) the effective valence does not change and is equal to 2.65. Above RT with increasing temperature the effective valence slowly increases up to 2.80 at 523 K.

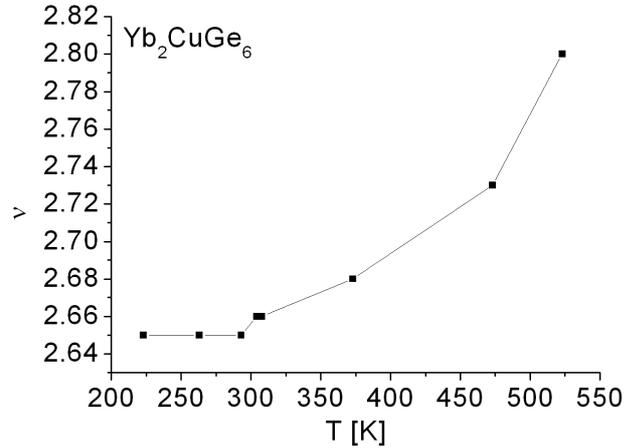


Fig. 4. Temperature dependence of the effective valence  $v$  of  $\text{Yb}_2\text{CuGe}_6$ .

The core level spectra of Cu and Ge were also analyzed. The Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  peaks are at 933.1 eV and 953 eV and do not change with temperature. The peaks corresponding to Ge  $3p_{3/2}$  and Ge  $3p_{1/2}$  at 121.5 and 125.5 eV were Ge  $2p_{3/2}$  and Ge  $2p_{1/2}$  at 1216.8 and 1247.8 eV. This data are in good agreement with the table data for pure elements [5].

#### 4. Summary

The results presented in the work indicate that  $\text{Yb}_2\text{CuGe}_6$  exhibit a mixed-valence character. The effective valence increases with increasing temperature. Similar dependence of  $v$  was observed in  $\text{YbCu}_4\text{In}$  [6].

The presented in the work results are in good agreement with the anomaly in unit cell volume and anomalous large value of the paramagnetic Curie temperature

observed for  $\text{Y}_2\text{CuGe}_6$  in work [7]. Also in isostructural  $\text{Yb}_2\text{NiGe}_6$  compounds the mixed-valence state is observed [8].

The Yb atoms occupy two nonequivalent positions with a small difference in the atomic surroundings. The Yb1 is surrounded by 10 Ge atoms, while Yb2 by 10 Ge and 4 Cu atoms. Along the orthorhombic  $c$ -axis, atomic planes are stacked, and each one is composed of one kind of element. The interatomic distances between an Yb atom and the surrounding Ge/Cu atoms in  $\text{Yb}_2\text{CuGe}_6$  increase with increasing temperature because with increasing temperature the lattice parameters increase. These suggest that the valence state of ytterbium results from the dissimilar strength of the interactions between Yb  $4f$  electrons and  $p$ -electrons of Ge atoms. The hole-occupation number  $n_n = v - 2$  determined directly from XPS data  $n_n = 1/(1 + \frac{13}{14} \frac{I(+3)}{I(+2)})$  increases with increasing temperature.

### References

- [1] M.B. Konyk, P.S. Salamakha, O.I. Bodak, V.K. Pecharsky, *Kristallographia* **33**, 838 (1988).
- [2] M.B. Konyk, O.I. Bodak, *J. Alloys Comp.* **387**, 243 (2005).
- [3] D.A. Shirley, *Phys. Rev. B* **5**, 4709 (1972).
- [4] S.-J. Oh, J.W. Allen, M.S. Torokachivili, M.B. Maple, *J. Magn. Magn. Mater.* **52**, 183 (1985).
- [5] S. Hüfner, in: *Photoemission Spectroscopy*, Springer-Verlag, Berlin 1994, p. 453.
- [6] F. Reinert, R. Classen, G. Nicolay, D. Ehm, S. Hüfner, W.P. Ellis, G.-H. Gweon, J.W. Allen, B. Kindler, W. Assmus, *Phys. Rev. B* **58**, 12808 (1998).
- [7] M.B. Konyk, L.P. Romaka, Yu.K. Gorelenko, O.I. Bodak, *J. Alloys Comp.* **311**, 120 (2000).
- [8] K. Shigetoh, F. Hirata, M.A. Avila, T. Takabatake, *J. Alloys Comp.* **403**, 15 (2005).