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Citation style: Szytuła A., Penc B., Konyk M., Winiarski Antoni. (2008).
Mixed-valence state in Yb_2CuGe_6 . "Acta Physica Polonica A" (Vol. 113, nr 4
(2008), s. 1205-1209).



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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 Yb_2CuGe_6

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

We present here temperature dependent X-ray photoemission measurements on polycrystalline Yb_2CuGe_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 Yb_2CuGe_6 compound investigated in this work belongs to the R_2TGe_6 family, where T is Mn, Ni and Cu. These compounds crystallize in an orthorhombic crystal structure of the Ce_2CuGe_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_α 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 Yb_2CuGe_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.

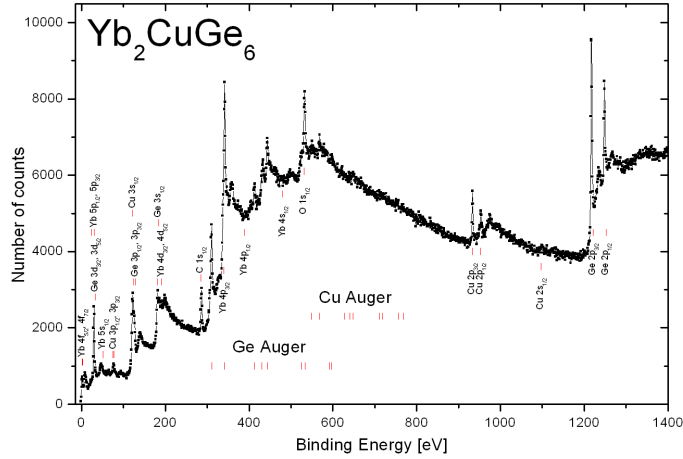


Fig. 1. XPS Al K_α spectrum of Yb_2CuGe_6 compound at room temperature in the wide binding energy range of 0–1400 eV.

The XPS valence bands (VBs) of Yb_2CuGe_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 Yb^{3+} part is comparable with that of the Yb^{2+} part, suggesting that the Yb atoms in the studied compound are in-between

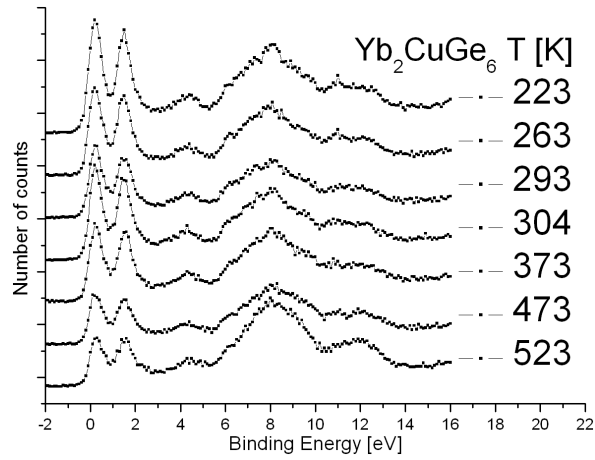


Fig. 2. XPS spectra of valence bands of Yb_2CuGe_6 in the temperature range 223–523 K.

divalent and trivalent states. With increasing temperature the intensity of the peaks corresponding to Yb^{2+} state decreases while the peaks corresponding to 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 Yb^{2+} while the peaks at 186 eV and those in the region of 195–210 eV correspond to Yb^{3+} . The intensity of the peaks corresponding to the Yb^{3+} state increases with increasing temperature.

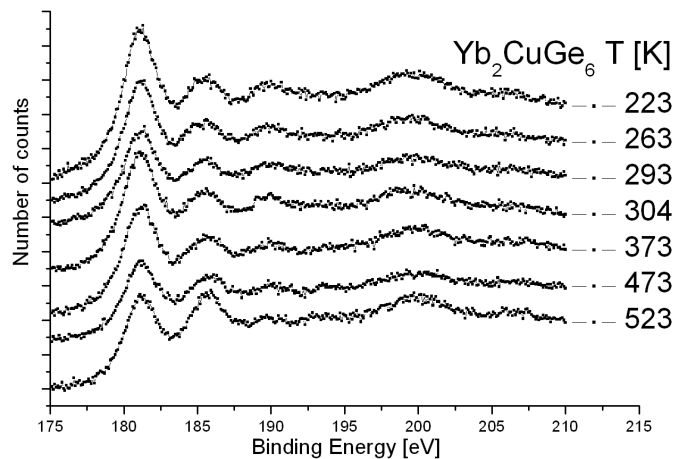


Fig. 3. Yb 4d core level photoemission spectra of Yb_2CuGe_6 as a function of temperature in the range 223–523 K.

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.

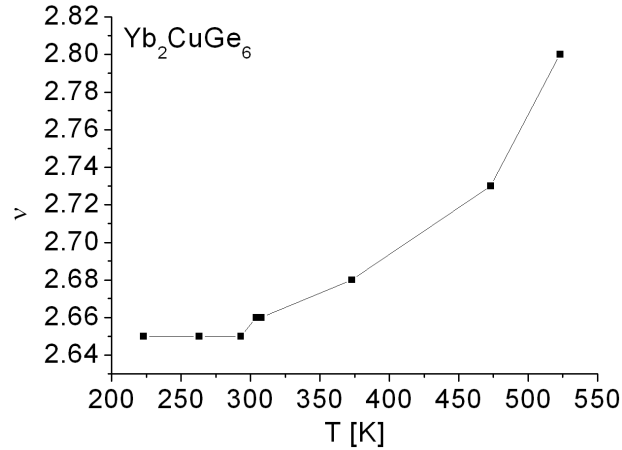


Fig. 4. Temperature dependence of the effective valence v of Yb_2CuGe_6 .

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 Yb_2CuGe_6 exhibit a mixed-valence character. The effective valence increases with increasing temperature. Similar dependence of v was observed in YbCu_4In [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 Y_2CuGe_6 in work [7]. Also in isostructural Yb_2NiGe_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 Yb_2CuGe_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.

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