ELECTRONIC STRUCTURE
OF UCo4B COMPOUND

A. Szajek*, L. Smardz, A. Szlaferek and A. Kowalczyk

Institute of Molecular Physics, Polish Academy of Sciences
Smoluchowskiego 17, 60-179 Poznań, Poland

　　　UCo_4B is a member of uranium intermetallic borides family which crystallizes in the hexagonal $CeCo_4B$ structure. The experimental data suggest the occurrence of the spin-fluctuation behaviour of UCo_4B. In this paper we present the results of band structure calculations using the *ab-initio* tight binding linear muffin-tin orbital method. We found good agreement between the experimental X-ray photoemission spectroscopy valence band spectrum and the *ab-initio* results.

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1. Introduction

　　　Compounds containing uranium have attracted much attention over the last decade. In contrast to $4f$ electrons in lanthanides, which in most cases are well localized, the $5f$ electrons in actinides exhibit a diversified behaviour. The overlap of the more extended $5f$ wave functions of neighbouring actinide atoms in solids leads to the delocalization of the $5f$ states. In elemental actinide metals structural and electronic properties can be understood assuming an increasing degree of localization with the increasing $5f$ occupancy. In an early systematics known as the Hill rule [1] it was conjectured that, for a spacing between actinide atoms lower than a certain critical value, direct $5f$–$5f$ overlap results in delocalization of $5f$ electrons. However, in many uranium compounds the dominating hybridization effects cause exceptions from the Hill rule [2].

　　　The uranium intermetallic borides are examples of very interesting compounds [3 and ref. therein]. One of them, the UCo_4B, crystallizes in the hexagonal $CeCo_4B$ structure. The lattice parameters obtained by X-ray diffraction [4] were: $a = 4.902$ Å and $c = 6.949$ Å. It means that the shortest distance d_{U-U} of uranium atoms in UCo_4B is about 3.475 Å. Following the Hill rule, the distance falls into the transition region from magnetic compounds d_{U-U} larger than 3.6 Å to non-magnetic compounds for d_{U-U} smaller than 3.4 Å.

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*corresponding author; e-mail: szajek@ifmpan.poznan.pl

In this paper we present a study of the electronic structure of hexagonal UCo_4B by the *ab-initio* linear muffin-tin orbital (LMTO) method. To probe the occupied part of the valence band the photoemission spectrum is calculated and compared with experimental X-ray photoemission spectroscopy (XPS) data.

2. Experimental and band calculations details

The UCo_4B compound was prepared by induction melting of stoichiometric amounts of the constituent elements in a water-cooled boat, under an argon atmosphere. The ingot was inverted several times to insure homogeneity. The sample was then heat treated at 1000°C for two weeks. The crystal structure was examined by the standard $\theta-2\theta$ X-ray diffraction technique using the Cu K_α radiation ($a = 4.9002$ Å and $c = 6.9428$ Å).

The XPS valence band spectra were measured with Al K_α radiation of 1486.6 eV at room temperature using a SPECS EA 10 PLUS energy spectrometer. The energy spectra of electrons were analysed by a hemispherical analyser ($FWHM_{MgK_\alpha} = 0.8$ eV for Ag $3d_{5/2}$). Calibration of the spectra was performed according to Baer et al. [5]. All emission spectra were measured immediately after the sample cleaning in a vacuum of 8×10^{11} mbar. The $4f_{7/2}$ peak of gold was situated at 84.0 eV and the Fermi level was located at $E = 0$ eV.

The band structure was calculated using the tight binding linear muffin-tin orbital (TB LMTO) method in the atomic sphere approximation (ASA) [6, 7], with the spin–orbit interactions taken into account in the form proposed by Min and Jang [8]. The Perdew–Wang [9] potential with gradient corrections was used. The standard combined corrections terms [6] were included to compensate for errors due to the ASA. The band structure was calculated for experimental values of the lattice constants. Computations were done for 484 k-points in the irreducible wedge of the first Brillouin zone. For integration over the Brillouin zone the tetrahedron method was used [10–12]. The iterations were repeated until the energy eigenvalues of the consecutive iteration steps were the same within an error of 0.01 mRy.

To probe the occupied part of the electronic band structure the photoemission spectrum was calculated. The XPS spectrum was calculated from the partial densities of states DOS(E) weighted with atomic photoemission cross-sections [13] for the photon energy being equal to 1486.6 eV (Al K_α source). The finite experimental resolution was taken into account in calculations by convoluting the weighted DOS(E) with an energy dependent Lorentzian function with a half-width $\delta = 0.5$ eV.

3. Results

In Fig. 1 the partial DOS curves are presented. The results show that the cobalt d-electrons provide the main contribution to the DOS for $E = E_F$. The value of the total DOS at the Fermi level is equal to 16.844 states/(eV · unit cell) which corresponds to the value of 19.871 mJ/(mol K^2) of the calculated coefficient γ_0 in the linear term of the specific heat. The experimental value of γ is equal to
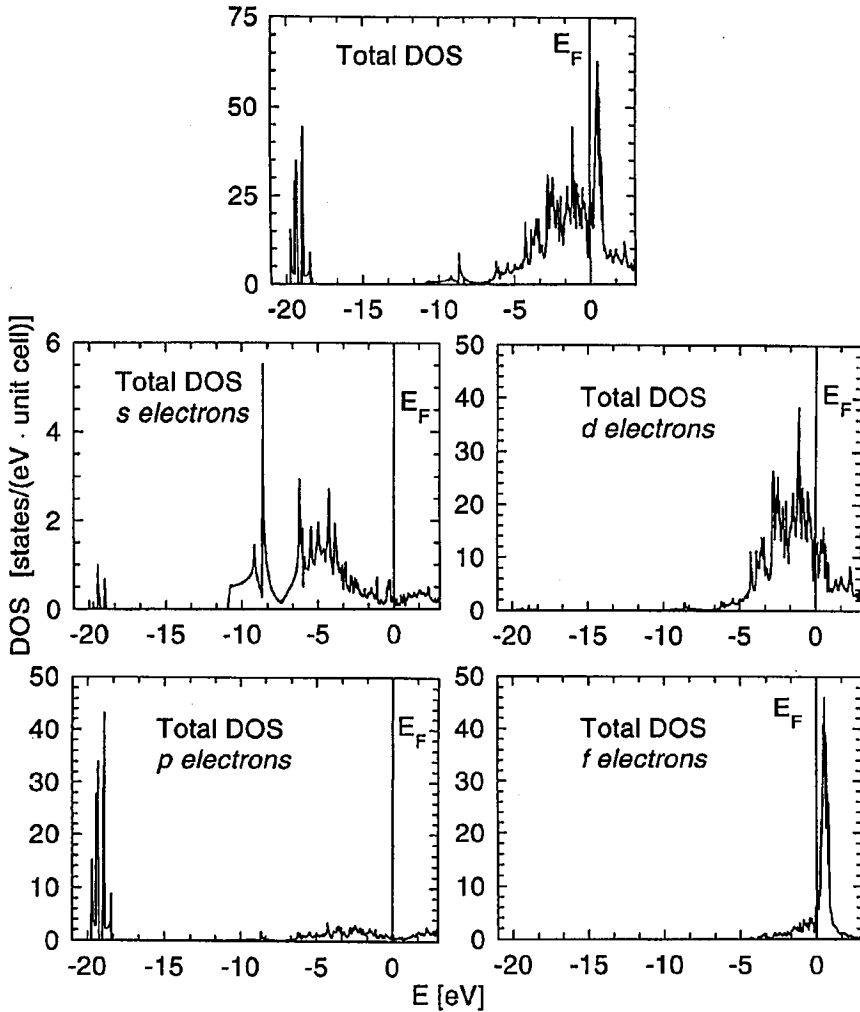
Fig. 1.   The total and *l*-decomposed DOS for UCo₄B.

62 mJ/(mol K²) [4]. It suggests that the mass enhancement factor λ is large. Its value can be calculated using the expression $\gamma = \gamma_0(1 + \lambda)$ and is equal to 2.124. The 5f electrons from the uranium sites form a wide band. As both the types of uranium atoms have about 3 electrons only, the band is not filled. The main part of the band is empty and its gravity centre is above E_{F}. The p electrons form two bands. The low energy band located around 19 eV below the Fermi level is split into two subbands because of the spin–orbit coupling. They are formed by p electrons localized on U atoms. The second part of the p-band is expanded from −11 eV up to the energies above E_{F}, and this band is formed by p electrons localized on Co and B atoms.
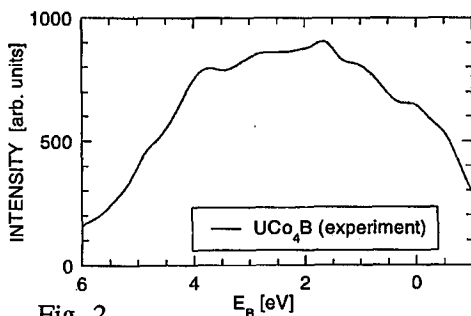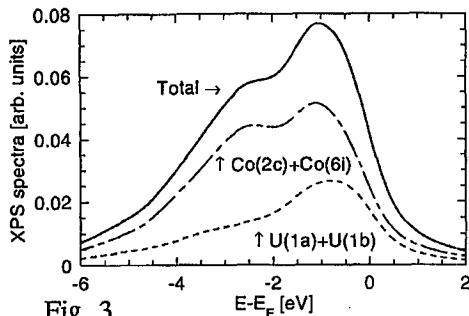
Fig. 2.

Fig. 3.

Fig. 2. The experimental XPS spectrum for the UCo_4B system.

Fig. 3. The calculated photoemission spectrum for the UCo_4B system and local contributions for particular atoms.

The experimental XPS spectrum presented in Fig. 2 shows the valence band in the range about 6 eV below the Fermi level. The main peaks are located at about 1.5 eV and 3 eV below E_F. The calculated photoemission spectrum presented in Fig. 3 has main peaks between $1 \div 1.5$ eV and $2.5 \div 3$ eV below E_F. Both types of Co atoms (2(c) and 6(i)) provide a large contribution to these peaks. The XPS peak from the uranium atoms is located in the lower-binding part of the spectrum because the $4f$ electrons are localized close to the E_F and provide relative large contributions to the DOS at the Fermi level. The contribution of the boron atoms is small and may be omitted because of the small number of electrons provided to the valence band and very small values of the cross-sections for the energy of radiation used in the experiment.

In conclusion, we have found good agreement between the experimental XPS valence band spectrum and the *ab-initio* calculations.

Acknowledgments

References

[1] H.H. Hill, in: *Plutonium and other Actinides*, Ed. W.N. Miner, AIME, New York 1970, p. 2.

[2] V. Sechovsky, L. Havela, in: *Ferromagnetic Materials*, Eds. E.P. Wohlfarth, K.H.J. Buschow, Vol. 4, North Holland, Amsterdam 1988, p. 309.

[3] G.J. Nieuwenhuys, *Phys. Scr. T* **49**, 278 (1993).

[4] H. Nakotte, L. Havela, J.P. Kuang, F.R. de Boer, K.H.J. Buschow, J.H.V.J. Brabers, T. Kuroda, K. Sugijama, M. Date, *Int. J. Mod. Phys. B* **7**, 838 (1993).

[5] Y. Baer, G. Busch, P. Cohn, *Rev. Sci. Instrum.* **46**, 466 (1975).

[6] O.K. Andersen, O. Jepsen, M. Šob, in: *Electronic Structure and its Applications*, Ed. M.S. Yussouff, Springer, Berlin 1987, p. 2.

[7] G. Krier, O. Jepsen, A. Burkhardt, O.K. Andersen, *The TB-LMTO-ASA Program* (source code, version 4.7, available upon request from the program authors).

[8] B.I. Ming, Y.-R. Jang, *J. Phys., Condens. Matter* **3**, 5131 (1991).

[9] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).

[10] O. Jepsen, O.K. Andersen, *Solid State Commun.* **9**, 1763 (1971).

[11] O. Jepsen, O.K. Andersen, *Phys. Rev. B* **29**, 5965 (1984).

[12] P. Blöchl, O. Jepsen, O.K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).

[13] J.J. Yeh, I. Lindau, *At. Data Nucl. Data Tables* **32**, 1 (1985).