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Photoemission spectroscopy of AT_4Sb_{12} (A=Ca, Sr, Ba; T=Fe, Ru, Os)

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Filled-skutterudite compounds have attracted a great interest because of the thermoelectric application as well as unusual physical properties. In comparison with rare-earth filled compounds, alkaline-earth filled ones have less been studied. Recently, Matsuoka *et al.* have prepared AT_4Sb_{12} (A=Ca, Sr, Ba; T=Fe, Ru, Os) polycrystals and investigated their magnetic and transport properties [1, 2]. In collaboration with them, we have started photoemission spectroscopy (PES) of AT_4Sb_{12} using synchrotron radiation in December 2004. In this workshop, we report preliminary results of the valence-band and Sb 4d PES spectra of AT_4Sb_{12} .

High density pellets were prepared by a spark-plasma sintering technique. The samples were characterized by x-ray diffraction measurements and electron-probe micro-analysis. Clean surfaces for PES measurements were obtained by fracturing. PES spectra were measured on the beamline BL7 at HiSOR using a hemispherical photoelectron analyzer (Gammadata-Scienta SES100). Total energy resolution was set to 120 meV at $h\nu=60$ eV. The experiments were carried out at room temperature with excitation energies of $h\nu=100$, 60 and 70 eV for T=Fe, Ru and Os, respectively, where PES spectra almost reflect T d density of states (DOS) due to energy-dependent photo-ionization cross-sections of photoelectrons [3].

From the valence-band PES spectra, we find that the T d bands shift toward deeper binding-energy side as going from T=Fe to Ru, and to Os. In particular, only for AFe_4Sb_{12} , the Fe 3d DOS largely contributes to the Fermi level (E_F). On the other hand, few DOS is observed at E_F for ARu_4Sb_{12} and AOs_4Sb_{12} compounds. The present experimental result is consistent with the results of electric specific coefficients; $\gamma \sim 100$ for AFe_4Sb_{12} and ~ 10 mJ/mol K² for ARu_4Sb_{12} [1]. The Sb 4d PES spectra of AOs_4Sb_{12} show multi-components on the deeper side of the Sb 4d_{5/2} and 4d_{3/2} main peaks, which are not observed for AFe_4Sb_{12} and ARu_4Sb_{12} . At present, it is not clear whether the origin is intrinsic and extrinsic. The further experiments are in progress and we will those results including high-energy resolution PES of AT_4Sb_{12} at next meeting.

[1] E. Matsuoka *et al.*, cond-mat/0412094.

[2] E. Matsuoka *et al.*, this workshop 6b5.

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