Application Note
Valence band spectroscopy using VUV5000

The change in line shape and peak positions of valence band photoemission (PES) spectra due to change in excitation energy can be attributed to cross sections. This fact can be used in valence band studies to assign features to specific element and orbital configurations, as done by the group of Professor Maiti, using HeI (21.2 eV) and HeII (40.8 eV) light for determining the valence band composition of the $EuFe_2As_2$ compound.

The measurements were performed at the lab of Professor Maiti using a high-resolution PES setup equipped with a Scienta Omicron R4000 WAL analyser and a Scienta Omicron VUV5k UV source. The VUV5k is an excellent tool for valence band studies, since light of 21.2 eV (HeI) and 40.8 eV (HeII) can be easily selected by changing the grating position of the monochromator.

$EuFe_2As_2$ is a pnictide with a superconducting phase due to FeAs layers with hybridized Fe-As orbitals. The study by Ganesh Adhikary et al. presented in Journal of Physics: Condensed Matter 25 (2013) 225701 is focussed on mapping the electronic structure of the $EuFe_2As_2$ compound above and below 20 K since the Eu-moments undergo an antiferromagnetic (AFM) ordering at this temperature. As a part of this study the valence band features is assigned to different orbitals of the compound elements. This application note describes the elegant method used in this paper for this assignment.

Valence band PES measurements of $EuFe_2As_2$ at 30 K for HeI and HeII excitation energies are displayed in Figure 1. There are two distinguished features in the spectra, denoted A and B. Feature A is located between 0 and 0.75 eV. The intensity maxima is located at higher binding energies for the HeI spectra compared to the He II spectra when they are normalized by the intensity maxima in this energy range. Feature B is located at around 1.0-2.5 eV. The intensity of this feature is significantly reduced for the HeI spectra compared to the HeII spectra. Using the ionization cross sections calculated by Yeh and Lindau (Atomic data and nuclear data tables 32 (1985) 1) we see that the cross section, and therefore the intensity, increases for Fe and Eu going from HeI to HeII excitation energy, whereas the cross section decreases for As (Table 1). Since the intensity of the feature A is stronger than that of B in He I spectrum compared to He II spectrum, the feature A must have As 4p orbital contribution.

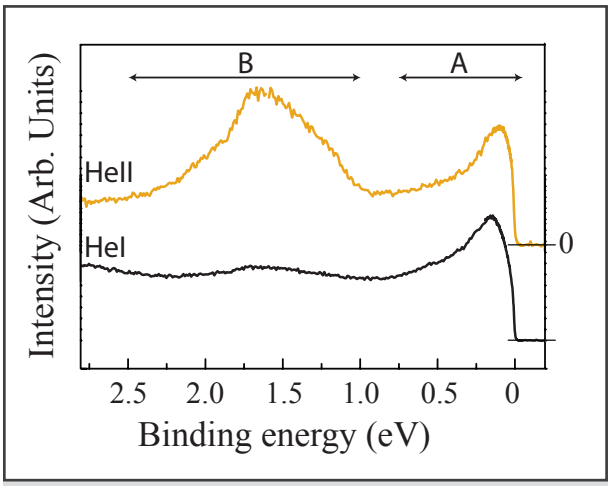

Figure 1: Valence band of the $EuFe_2As_2$ compound recorded with HeI (21.2 eV) and HeII (40.8 eV) light. Two distinct features, denoted A and B can be identified for the spectra.

Since the hybridized electronic states are often successfully captured by the linear combination of the atomic orbitals, the cross-section ratio between He I and He II would follow the trend of the cross sections of the individual atomic orbitals. Thus, we can conclude that feature A has a As 4p -Fe 3d character, well in line with what is known about the material being made up of to FeAs layers that have hybridized Fe-As orbitals. Feature B decrease in intensity going from HeII to HeI excitation, which fit well with the nature of the cross section for the Eu 4f. It is therefore possible to conclude that peaks B stem from Eu 4f.

Compound orbital	Cross section @ 21.2 eV (Mb)	Cross section @ 40.8 eV (Mb)	Change HeI/HeII
Fe 3d	4.833	8.761	0.55
As 4p	3.856	0.2949	13
Eu 4f	0.6312	2.986	0.21

Table 1: Cross section of Fe 3d, As 4p and Eu 4f in 106 barns from J. J. Yeh and I. Lindau, Atomic data and nuclear data tables 32 (1985) 1.

By closer examination of the Fe 3d As 4p hybridized feature A it is possible to identify 3 different peaks, denoted A1, A2 and A3, shown in Figure 2. A1 appears at 50 meV, A2 at 200 meV and A3 at around 500 meV. A1 Shows about the same intensity for HeI and He II light whereas A2 and A3 are present only for the HeI excited spectrum. From table 1 it is possible to deduce that the p orbital character will be stronger for the HeI excitation energy while the d characters will be stronger for HeII light. Thus, it is possible to conclude that A1 has mixed p-d character and A2 and A3 has p character. This study shows that conduction electrons near Fermi level has strong p-character and are influenced by the Eu-magnetism although $EuFe_2As_2$ become superconducting on application of pressure or doping.

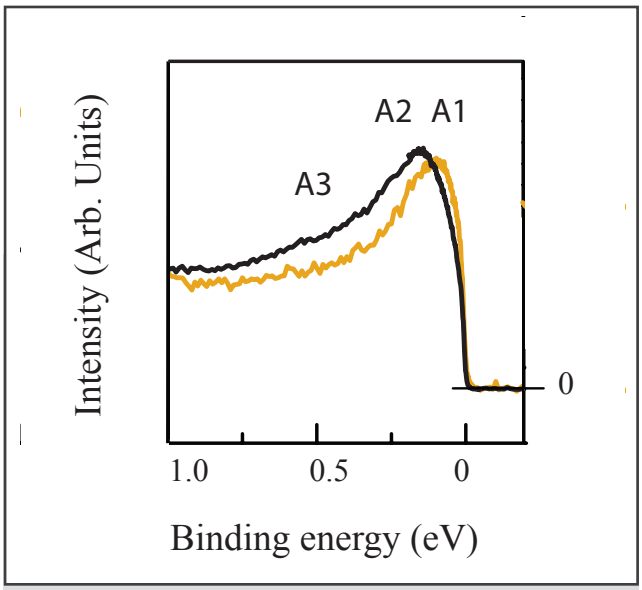

Figure 2: Zoom in on feature A of the valence band of the EuFe2As2 compound recorded with HeI (21.2 eV) and HeII (40.8 eV) light. Three features can be identified, here denoted A1, A2 and A3.

This application note was written in collaboration with Professor Kalobaran Maiti, Tata Institute of Fundamental Research, India, and based on the article by Ganesh Adhikary et al. presented in Journal of Physics: Condensed Matter 25 (2013) 225701. For further questions please contact kbmaiti@tifr.res.in.