Free one- and bicomponrent metal clusters
studied by synchrotron-based photoelectron spectroscopy

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In a pair of recent years significant progress has been made by us in the field of *free* metal nanoscale clusters using photoelectron spectroscopy. This progress has been possible due to the combination of an efficient gas-aggregation cluster source, the high-flux tunable x-ray radiation at MAX-lab synchrotron facility, and the versatile end-station of the beamline. The metal vapour in the cluster source is produced either by resistive heating of a furnace or by magnetron sputtering inside a liquid-nitrogen cooled cryostat. So far a number of materials were successfully used by us for *free* nanoscale cluster production and *core-level* spectroscopy on them: Na, K, Pb, Bi, Sn, and –very recently- Mg and Au. Additionally, for Cu, Ag, Na, K, Pb, and Au clusters the electron density of states was mapped by means of the valence photoelectron spectroscopy. Among the most recent achievements one can name successful production and characterization of free metallic core-shell clusters out of sodium-potassium alloy (figure 1,2), and doping of free potassium clusters with favourably chosen gas-phase molecules. For the Na-K clusters our XPS study disclosed the dominating presence of potassium- metal with the lower surface energy – on the surface, and sodium in the bulk of the clusters. This result has been possible to obtain due to the provided by the core-level photoelectron spectroscopy capability to get separate responses from the bulk and surface atoms of a cluster containing a few thousand atoms. Due to the same experimental capabilities it has been possible to record a well-resolved signal from potassium atoms on the cluster surface on which the molecules of the doping gas have adsorbed. Among other achievements of the recent past are the XPS studies of plasmons in free Na, K and Mg clusters, pointing at the overwhelming extrinsic nature of the bulk plasmons. Auger and XPS spectroscopy has been successfully implemented to free potassium clusters what allowed to use the so-called Auger parameter method for estimating the degree of screening of the core-hole by the valence electrons in a free metallic cluster of a few thousand atom size. Among other achievements one can mention the demonstrated possibility to probe the deeper core levels of free metallic clusters. This has been demonstrated for potassium cluster 2p levels and for the lead cluster 4f levels. The presentation will give an overview of the experimental methods, the ways to use the obtained XPS and Auger spectra for deriving information on the cluster size, charge states, energy structure, details of the core-valence electron interaction, multielectron phenomena like plasmons, etc.

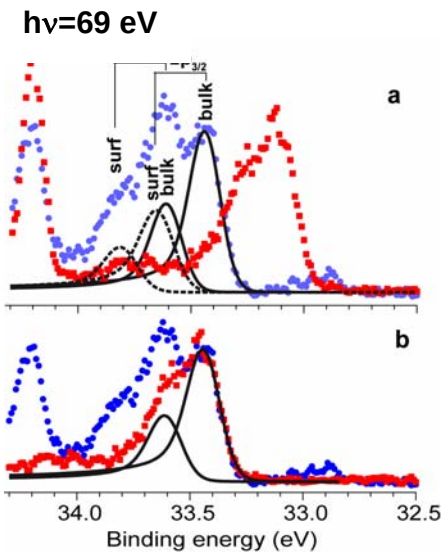

Fig.1 (to the left) Sodium cluster XPS spectrum for the pure case (circles), and for the mixed Na-K case (squares). In the **b** part of the figure the mixed-case spectrum is shifted up to align the lower binding energy flanks, and thus to demonstrate different widths of the features.

Fig.2 (to the right). **a**- "alloy" and **b**- "pure" cluster responses in the potassium 3p binding energy region. The fit for the pure-metal case with the spin-orbit and bulk and surface components is also given.